AN INTRODUCTION

TO

HARMACEUTICAL AND MEDICAL

CHEMISTRY.

AN INTRODUCTION

TO

PHARMACEUTICAL AND MEDICAL CHEMISTRY.

PART I.

(Theoretical and Descriptive).

ARRANGED ON THE PRINCIPLE OF THE

COURSE OF LECTURES ON CHEMISTRY,

AS DELIVERED AT THE

SOUTH LONDON SCHOOL OF PHARMACY.

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PREFACE TO THE SECOND EDITION.

IN issuing the second edition of this work, I determined to collect all the theoretical and descriptive portion together in one part, and the practical portion in another part, so that if deemed advisable it could either be issued in one or could be divided and bound in two volumes, one for home use and the other for the laboratory. Each portion is thus kept distinct with its own index so as to facilitate ready reference, and I sincerely trust that in its altered form the work will at once prove more handy to students, and be received with the same favour as that already extended to the "first" and "revised" editions.

As before, I am indebted to my friend Mr. Joseph Ince for his assistance in proof reading and in compiling the copious indices.

J. M.

WINCHESTER HOUSE,
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CHAPTER I.

INTRODUCTION.

I. MATTER AND ITS VARIOUS STATES OF EXISTENCE.

The subject of Chemistry is matter. By matter we mean everything which we see, feel, taste, or smell; in short, anything which affects our senses. All matter exists in one of three states:—

1. **Solid.**—In which condition the ultimate particles or molecules are closely pressed together, and which is consequently the least porous and mobile form of matter, requiring, as a rule, to be cut or pressed so as to suit its size to any particular vessel in which it is desired to be placed.
2. **Liquid.**—In this state, the molecules are not so closely pressed, but can move freely about each other. Liquids are consequently more porous than solids, and of themselves assume the form of any receptacle into which they are introduced.
3. **Gaseous.**—Matter in the gaseous state is the most porous, and the molecules appear to have so little attraction for each other that they would become altogether dissociated, were it not for the pressure exercised by surrounding bodies. The integral particles of gases are considered as being in continual movement. One solid body placed against another refuses to mix with it except by continual pulverization; liquids mix more readily, with a slight amount of stirring; while gases mix of their own accord. This property takes place by a fixed law, called the *law of diffusion*, which is usually stated as follows:—*Gases mix with each other of their own accord at a rate which is inversely proportioned to the square root of their relative densities.* Thus, the density of hydrogen being 1, and oxygen 16, the square roots are respectively 1 and 4; and by inverse proportion, we see that hydrogen will diffuse itself in oxygen four times as quickly as the latter will mix with hydrogen. Gases also possess in an eminent degree the property of *elasticity*, that is, they may be reduced to a smaller volume by pressure, but immediately on its removal they will assume their original bulk. The greater the pressure the less the volume of gas; and the less the pressure the greater the volume.

There are certain general properties which all matter shares in common.

1. **Extension.**—By this we mean that every body occupies a certain bulk, or that it must have a certain degree of length, breadth, and thickness, irrespective of its form or of how that form may be changed.
2. **Impenetrability,**—which signifies that no two bodies can occupy the same space at the same time.
3. **Indestructibility.**—We may change and decompose matter as we please, but we cannot destroy the minutest particle.

4. **Porosity.**—All bodies, no matter how hard in appearance, are nevertheless porous; consequently we can alter and modify their shape and size by heat, pressure, and other means.
5. **Inertia.**—By this term is indicated the fact that matter is incapable of either setting itself in motion or arresting its own progress when in movement.
6. **Divisibility.**—All substances are capable of separation into minute particles, and the extent to which this division may be carried with some compounds is remarkable. For instance, a pail of water holding two gallons may be distinctly coloured with *one grain* of indigo dissolved in sulphuric acid, and yet each grain of the water in the vessel will only contain $\frac{1}{140000}$ part of a grain of the pigment. Here the question arises, Is matter really infinitely divisible, or is there a point at which divisibility ceases? The latter view is in the present state of science most commonly held to be the correct hypothesis; all matter being conceived as the aggregate of certain inappreciable particles named **molecules**, which in turn are derived from the union of infinitely more minute portions of elements called **atoms**. The *atom of an element is therefore held to mean the smallest quantity capable of existence, and is considered absolutely indivisible.*

Matter in the condition in which it is perceptible to our senses is said to be in the *free state*, and since, previously to its detection by our organs of perception, it must consist of myriads of atoms, it is believed that *atoms cannot exist in this free state, but that they must be combined with other atoms of the same or of a different element in order to form molecules, which alone can assume that condition.* If, therefore, we wish to express that an element, hydrogen, for example, is in a free state, we must not write simply H, but H_2; thus intimating that *at least two atoms have coalesced to produce a molecule capable of existing in the free state.*

II. ANALYSIS AND SYNTHESIS. ELEMENTS AND SYMBOLS.

With regard to matter, the chemist makes two inquiries; 1st: What are its ingredients? and 2nd: Having isolated such constituents, how are they to be combined so as to reproduce the original substance? The process by which an answer is obtained to the former question is called **analysis**; and to the latter, **synthesis.**

Analysis is the chemical pulling to pieces of a substance in order to discover its component parts, whilst synthesis is the building up of a compound from its ingredients. For example: If we take a piece of alum and submit it to analysis, we can prove that it contains oxides of aluminium and potassium, sulphuric anhydride, and water. If we then take these substances and separately analyze them, we find that they in turn consist of aluminium, potassium, sulphur, oxygen, and hydrogen; but a further attempt to analyze this last group ends in failure. We have reduced our alum to certain ingredients which defy our best efforts to ascertain of what they are composed The result of analysis, therefore, has been to acquaint us with a certain number of simple bodies which we call "*elements*," by the mutual combination of which all matter is formed. When we use the term "simple bodies," the student must understand that the elements are not really to be so considered in the fullest sense of the word. They are only so regarded, because our present state of knowledge fails to enable us to discover their ultimate composition.

There are about sixty five of these simple bodies or elements known; but as many of them have no practical or commercial use, the pharmacist has really to do with only about thirty eight.

By universal consent, each element is represented by an appropriate letter, or a combination of letters, so that chemists adopting this arrangement may invariably understand what element is meant by a written **symbol**. The conception of expressing simple bodies by means of symbols is by no means modern, but dates back to the days of the alchymists. Thus, gold was represented by a rough drawing of the sun; while an equally uncouth sketch of a half moon denoted silver.

The names of the elements at present are purely arbitrary, and have been bestowed by the discoverers from some fancied special property: such as the designation *hydrogen*, derived from two Greek words, signifying "to beget water." The following is a list of the elements used in Pharmacy with their symbols, the committing of which to memory is the first duty of the learner:*

Elementary Bodies		Symbols	Elementary Bodies.		Symbols.
Aluminium		Al.	Iron	(*Ferrum*)	Fe.
Antimony	(*Stibium*)	Sb.	Lead	(*Plumbum*)	Pb.
Arsenic		As.	Lithium		L.
Barium		Ba.	Magnesium		Mg.
Bismuth		Bi.	Manganese		Mn.
Boron		B.	Mercury	(*Hydrargyrum*)	Hg.
Bromine		Br.	Nitrogen		N.
Cadmium		Cd.	Oxygen		O.
Calcium		Ca.	Phosphorus		P.
Carbon		C.	Platinum		Pt.
Cerium		Ce.	Potassium	(*Kalium*)	K.
Chlorine		Cl.	Silver	(*Argentum*)	Ag.
Chromium		Cr.	Sodium	(*Natrium*)	Na.
Copper	(*Cuprum*)	Cu.	Sulphur		S.
Gold	(*Aurum*)	Au.	Tin	(*Stannum*)	Sn.
Hydrogen		H.	Zinc		Zn.
Iodine		I.			

III. PRELIMINARY NOTICE OF FOUR TYPICAL ELEMENTS.

All the elementary bodies will be duly considered, and carefully described in their proper places, but meantime, the student may familiarize himself with a few preliminary facts about the most common elements as follows:—

1. **Oxygen.**—Take a few crystals of potassium chlorate, and having gently rubbed them to powder in a clean mortar, place the powder in a perfectly clean and dry test tube, and apply the heat of a Bunsen burner. The contents of the tube will fuse and then the liquid will be seen to effervesce, and a colourless gas will be given off. This is the element oxygen in the free state, and its presence may be shown by holding the end of a piece of stick in the gas flame until it is well burned, then blowing out the flame and holding the incandescent point just over the mouth of the tube. Oxygen being the great supporter of the combustion of organic bodies, the spark will glow

* The entire list of elements will be found in the Appendix.

with great brilliancy, and once more burst into flame. It is to the fact of oxygen being a constituent of the air we breathe, that we owe the support of our life, which is, after all, only a slow combustion. When we inhale air into our lungs the oxygen passes into the blood, and unites with some of the carbon to form carbonic acid gas, which is then exhaled. Oxygen is colourless and inodorous, and, although it supports the combustion of carbonaceous matter, it will not itself inflame in contact with the air. It can only be reduced to a liquid under an immense pressure, and even then only appears as a fog in the tube when the pressure is suddenly released so as to produce intense cold.

2. **Hydrogen.**—Place a few fragments of zinc in a small bottle, add a little water and then some sulphuric acid, when a powerful effervescence will take place, and a colourless gas will be evolved. This is the element in question in a free state. Now procure a cork which will well fit the neck of the bottle, and by means of a round file, make a hole through it. Into this hole a short glass tube, drawn out so as to form a jet, is tightly fitted, and the bottle is then closed by the cork so that the gas issues from the jet, and when the whole of the air has been expelled from the bottle, cautiously apply a light. Perfect safety may be ensured by first collecting portions of the gas in a small test-tube placed upside down over the end of the jet. Apply a light to ascertain the presence of the gas. Faraday recommended that the bottle should not be too large, so that the atmospheric air might easily "be swept out of the space above the water." The hydrogen will take fire and burn with a very feebly luminous bluish flame. This flame depends on the union of the hydrogen with the oxygen of the air to form steam, which fact can be proved by holding a cold glass shade over the flame, when the steam produced will be condensed into water and form in drops on the glass. The flame of hydrogen, although feebly luminous, is exceedingly hot, as may be seen by holding a fine platinum wire in it, when it will become intensely incandescent. A small fragment of lime will also be strongly heated, and it is thus that the lime light is produced, with the exception that oxygen and hydrogen are mixed just before combustion, and the flame urged upon the cylinder of lime by pressure. Hydrogen is colourless and inodorous, and, although it will thus burn in the air, a lighted match suddenly plunged into a bulk of the pure gas will be extinguished. With regard to ordinary combustion, hydrogen is thus exactly the reverse of oxygen. Like oxygen, it can be liquefied, but at a pressure even more extreme.

The elements just described are respectively the types of the two great classes into which elements are divided. As will be afterwards more fully explained, we have:—(1) The metallic elements, typified by hydrogen, which usually form the basylous or electro-positive portion of compounds; and, (2) The non-metallic elements, or metalloids, which, either by themselves or when united with oxygen, form the acidulous or electro-negative part of compound matter. Just as hydrogen and oxygen are typical of the opposing forces of elementary matter, so is the water produced by their combination typical of compound matter, made up by the union or mutual saturation of the opposing elementary forces.

3. **Nitrogen.**—Take a soup-plate and nearly fill it with water. Put a fragment of phosphorus in a small porcelain crucible and carefully float it on the surface of the water. Apply a light to the phosphorus, and quickly invert over it a receiver or a large beaker. The phosphorus will continue to burn until all the oxygen of the air in the beaker is

abstracted, when it will be extinguished, and the receiver will be filled with white fumes of phosphoric acid (anhydrous) formed by the union of the phosphorus with the oxygen. After the whole has stood for a few minutes these white fumes will dissolve in the water and disappear, and only a colourless gas will be left in the receiver. This is nitrogen in a free state, separated from the oxygen with which it was mixed, *not combined*—in the air we breathe. It is noticeable that at the conclusion of our experiment the water has been observed to rise in the receiver, and what was originally all air, is now only four-fifths nitrogen, the remaining space being occupied by the water which has taken the place of the oxygen. This shows us that our atmosphere is mainly a mixture of one-fifth of oxygen and four-fifths of nitrogen. Now introduce a light into the gas, it goes out, and the gas itself does not take fire, therefore nitrogen is neither combustible like hydrogen, nor is it a supporter of ordinary combustion like oxygen. Of what use then is it in the air? Why, simply as a perfectly neutral and negative body acting as a diluent of the activity of the oxygen. Nitrogen is an important constituent in the food of animals and plants, and all those curious and highly active bodies the vegetable alkaloids are rich in it.

4. **Carbon.**—Take some ordinary animal charcoal and wash it free from mineral impurities by hydrochloric acid, as directed in the Pharmacopœia under *Carbo animalis purificatus.* The resulting black powder is the nearly pure element in the free state. Heat a little of the powder on a piece of platinum foil; it glows and burns away. This is owing to its uniting with the oxygen of the air to form carbonic anhydride, which is a heavy colourless gas soluble to some extent in water, and when passed into *liquor calcis* turns it milky, owing to the formation of an insoluble compound called calcium carbonate. All organic matters contain carbon; and, in fact, the study of the compounds of carbon, other than metallic carbonates, is usually known as *organic chemistry.* To prove this, take an ordinary tallow candle and light it, when it appears to burn away; but this combustion is nothing more than the combination of the carbon and hydrogen of the tallow with the oxygen of the air, to form carbonic anhydride and water respectively. Invert a perfectly dry wide-mouthed bottle over the flame and hold it there until the flame is extinguished; then quickly insert the stopper and notice that a deposit of moisture has taken place on the glass, owing to the condensation of the water above mentioned. Next introduce a little clear *aqua calcis* and shake, when a deposit of calcium carbonate will be formed, proving the presence of the carbonic anhydride. All ordinary combustion is therefore due to a chemical action between the burning body and the oxygen of the air, so violent as to heat the body to such an extent that it becomes luminous. Candle and ordinary gas flames thus produced are hollow, and consist of three distinct zones. (1) The inner portion, where no combustion is going on, but which is simply filled with the combustible matter volatilized by the heat. (2) The luminous portion, or zone of imperfect combustion, in which the carbon has become deposited and highly incandescent. This is explained by the fact that when carbon and hydrogen are burnt together, the latter has a much more powerful attraction for the oxygen, and burns first, especially when, as in the present case, the air only plays round the outside of the flame. Thus, some of the hydrogen being abstracted, the carbon and the remainder of the hydrogen deposits as *soot* (a mixture of compounds of C and H rich in carbon) which becomes incandescent and gives the light. (3) The outer portion, or zone of perfect

combustion, which is a pale and almost invisible coating enclosing the entire flame, where the whole of the carbon and hydrogen unites with the oxygen of the air and produces intense heat. When the air is partly mixed with the gas before arriving at the point of ignition, the middle zone is supplied with sufficient oxygen from the interior to aid the air in fully burning it at once, and thus, although luminosity is sacrificed, the chemical action is more complete and the flame consequently much hotter. This is the principle of the *Bunsen burner*, which is fully described hereafter. (See the Author's **Analytical Chemistry**, Chap. I., page 25.)

Carbon also exists in the form of the diamond and of graphite, or plumbago ; and elements which are capable of thus assuming a number of forms totally distinct in physical appearance and properties, are said to be **allotropic bodies.**

Having thus familiarized himself with a few facts about the four most common elements, the student may proceed to study the first principles of the theories of chemistry and the notation based thereon.

CHAPTER II.

THEORIES OF CHEMICAL ACTION AND THE MODES OF EXPRESSING THE SAME BY FORMULÆ AND EQUATIONS.

I. LAWS OF COMBINATION.

The idea that matter is composed of atoms is very ancient, as we find it expressed by Democritus and other Greek philosophers; but no definite system as to the combination of atoms had been established until about 1804, when the researches of the eminent English chemist, Dalton, enabled him to lay down the following laws, which form the basis of all our present notions of chemical combination :—

1. Atoms combine with each other in a fixed and definite proportion by weight and volume.
2. As compound bodies are produced by the union of a given number of such atoms, it follows that the molecules of these compounds must also possess in their turn a fixed and definite combining proportion by weight and volume.
3. If a body can unite with another in more than one proportion, these proportions, which only represent the weights of the several atoms, must necessarily be simple multiples of the weights of any one of them. These laws are usually stated as follows :—

i. **The Quantitative Law.**—A definite compound always contains the same elements in the same fixed proportion.

ii. **The Law of Multiples.**—When the same bodies combine in more than one proportion, the resulting compounds contain a fixed proportion of one element in a varying proportion of the others; the second, third, and fourth proportions, etc., of the latter being always simple multiples of the first.

iii. **The Law of Reciprocal Proportions.**—The proportions in which any two elements unite with a third are the same proportions in which they unite with each other, or multiples of these proportions.

As an example of the first law, let us take water. No matter from what source it may be obtained, spring, river, or rain, it invariably contains oxygen and hydrogen in the relative proportions of 16 of the first to 2 of the latter by weight. An instructive example of the second rule is found in the compounds of oxygen and nitrogen. The simplest relation in which those bodies combine is 28 of nitrogen and 16 of oxygen. The next compound contains 28 of nitrogen and 32 of oxygen; the third, 28 of nitrogen and 48 of oxygen; the fourth, 28 of nitrogen and 64 of oxygen; and the fifth, 28 of nitrogen and 80 of oxygen. Thus, dismissing the nitrogen, which remains constant, let us look at the numbers 16, 32, 48, 64, 80 : are they not all multiples of 16,

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the simplest proportion? As an example of the third law:—Chlorine unites with hydrogen in the proportion of 35·5 to 1, and iodine also unites with hydrogen in the proportion of 127 to 1; therefore, chlorine combines with iodine in the proportion of 35·5 to 127. Seeing that these combining proportions by weight are only relative, it follows that they must all be referred to one standard; and as *hydrogen is the lightest known body in nature, it is taken as unity*, when other bodies are found to combine with it in the following proportions by weight, *which figures it is necessary to commit to memory*:—

Hydrogen . . . *H.* . . . . 1.

Elementary Bodies.	Combining or Atomic Weights.	Elementary Bodies.	Combining or Atomic Weights.
Aluminium	27·5	Iron	56
Antimony	122	Lead	207
Arsenic	75	Lithium	7
Barium	137	Magnesium	24
Bismuth	210	Manganese	55
Boron	11	Mercury	200
Bromine	80	Nitrogen	14
Cadmium	112	Oxygen	16
Calcium	40	Phosphorus	31
Carbon	12	Platinum	197
Cerium	92	Potassium	39
Chlorine	35·5	Silver	108
Chromium	52·5	Sodium	23
Copper	63·5	Sulphur	32
Gold	196·5	Tin	118
Iodine	127	Zinc	65

If we take a pint of hydrogen and a pint of oxygen, a pint of nitrogen and a pint of chlorine (all measured at the same temperature and pressure), we shall find that although the bulks are equal, the oxygen weighs 16 times, the nitrogen 14 times, and the chlorine 35·5 times as much as the pint of hydrogen. We conclude, therefore, from this simple experiment that matter in the state of vapour (its simplest condition) is equal in volume but different only in weight; and what is thus proved to be true as to a given volume, is viewed as also holding good with regard to the individual atoms which compose that volume. Hence it is reasoned that the atoms of the elements, *although equal in bulk, differ in weight*, and that the combining proportions referred to in the above table must be *the actual difference in weight of the individual atoms themselves*. Acting upon this theory, these proportions are called the **atomic weights** of the respective elements. That those combining proportions are really the true atomic weights of the various elements, is considered to be proved by physical as well as chemical means. The amount of heat required to raise equal quantities of various bodies through one degree of temperature is called their **specific heat**. If this specific heat be taken, as compared with that of water, as unity, it is found that bodies so examined give a series of numbers without any apparent connection; but if the **atomic heats** of the elements be taken (that is the amount of heat required to raise atomic weights of the respective bodies through one degree) it is found that nearly all elements give a similar result. In other words,

that when the specific heats of the elements are multiplied by their atomic weights an almost equal product is obtained. The following table will illustrate this uniformity:—

ELEMENTS.	SPECIFIC HEAT.	ATOMIC WEIGHT.	SPECIFIC HEAT × ATOMIC WEIGHT.
Sodium	0·2934	23	6·75
Potassium	0·1696	39	6·61
Bromine	0·0843	80	6·75
Iodine.	0·0541	127	6·87
Mercury	0·0333	200	6·66
Tin	0·0562	118	6·63

If we extend our researches from elements to compounds, we find that equal volumes of compound gases also differ in weight in the same fixed manner. This difference is therefore regarded as representing the relative weights of the molecules of the compound; and for similar reasons to those already given, *the combining weight of a compound body is called its* **molecular weight,** *and is always equal to the sum of the atomic weights of its constituent elements.* Thus, one molecule of hydrochloric acid consists of 1 atom of chlorine weighing 35·5 and 1 atom of hydrogen weighing 1; the molecular weight of this acid is therefore 36·5. From these explanations it follows that we are always to speak of the combining proportions by weight as the *atomic weights of elements,* and the *molecular weights of compounds* or of *elements in a free state.*

II. CHEMICAL ACTION.

This action is characterized by the grand distinction, that whenever it is induced a complete change is caused to take place in the bodies affected. It is by this thorough transmutation that true chemical energy is invariably recognised, in contradistinction to the tame effect resulting from a merely mechanical mixture. For example:—If we rub together some sugar and potassium chlorate we obtain a white powder, in which the ingredients are intimately mixed together, but are not in a state of chemical union; for by digesting the powder in spirit we can dissolve the sugar, leaving the potassium chlorate exactly as it was. Let us now add to the same powder a drop of sulphuric acid, and watch the astonishing result. The whole mass instantly inflames; a cloud of steam arises, and a black residue is left, from which no human dexterity can recover the original sugar or potassium chlorate. This experiment illustrates a true chemical combination, involving an entire change in the bodies acted upon.

Chemical action is always accompanied by an alteration in the temperature of the substances combining, and frequently an appreciable amount of heat and even light is produced. The tyro who desires to be made sensible of the heat produced by chemical action, has only to grasp a test-tube containing water, and add quickly about one sixth of strong sulphuric acid, when he will receive a convincing proof of this assertion. Many circumstances affect the rapidity and even determine the occurrence of chemical action. Chief among these is *solution.* This is exemplified in the ordinary granulated citrate of magnesia, as it is erroneously named, but which, as commonly sold, is chiefly a mixture

of tartaric acid and sodium acid carbonate. The mixture remains without change until dissolved in water, when a violent effervescence occurs, the ingredients combining to form a new substance, called sodium tartrate. Next to solution, *heat* is probably the most potent inducer and assistant to chemical action. We may rub a fragment of sulphur against a bar of iron for any length of time without affecting either; but let us heat the iron to whiteness, and apply the sulphur, and iron sulphide will be at once produced; a substance having no chemical resemblance to either of the ingredients used. Chemical action manifests itself much more strongly between certain bodies than between others, and it is by reason of this property that we are enabled to produce one compound from another. For example:—If we mix a solution of mercuric chloride and potassium iodide together in proper proportions, a bright scarlet substance quickly forms, and sinks to the bottom of the liquid. This is mercuric iodide, and its formation has been accomplished by chemical force. The mercury has a much greater affinity for iodine than the potassium possesses; consequently, the former displaces the latter, and unites with the iodine. This result could not occur except by reason of the superior manifestation of chemical force between the atoms of mercury and iodine. There are cases, however, in which the force between certain elements is so nearly balanced, that a slight change of circumstances is sufficient to determine in what direction the action shall be manifested. For example:—Oxide of iron heated to redness in a tube, and hydrogen gas passed over it, becomes reduced to metallic iron; while its oxygen, combining with the hydrogen, produces steam. If, however, the process be reversed, and steam be passed over the heated metal, oxide of iron will result, and hydrogen will escape. Thus we see that the chemical force acting between the elements is so nearly equal that the presence of an atmosphere of either hydrogen or steam is sufficient to determine the direction of the action. There is a very singular aid to chemical action, called **catalysis,** wherein the mere presence of a substance induces or hastens chemical action, the catalytic substance itself remaining perfectly unchanged and apparently in a neutral state. For example, if we heat potassium chlorate, it does not evolve oxygen until a tolerably high temperature has been attained; but should we previously mix a little manganese peroxide with the potassium chlorate, the gas is liberated at a much lower degree of heat. The manganese apparently has undergone no change, and yet, by its presence, has hastened the decomposition of the potassium chlorate. Catalysis has been accounted for by supposing that any element may exercise an influence over another element, even when circumstances entirely preclude the formation of a definite combination. Thus, in the above example, the metal manganese possesses an attraction for an additional atom of oxygen over the two already contained in manganese peroxide; and although, at a raised temperature, that third atom cannot actually be brought into union, yet the attraction so exercised causes the oxygen to be much more readily set free from the potassium chlorate than it would otherwise be.

III. COMBINATION OF GASES BY VOLUME.

We have already seen that equal volumes of elementary gases differ in weight exactly in the same ratio as their atomic weights. The weight of any portion of matter, compared with that of an equal bulk of another portion taken as a standard, is called its **specific gravity.** In the cases of liquid or solid bodies, their specific gravity is taken as referred to the standard of an equal bulk of distilled water at a fixed temperature; but in the case of gases we use hydrogen measured and weighed at 0° Centigrade (French thermometer) and 760

millimetres pressure (French barometer) as a standard of comparison, and when so taken the specific gravity is usually called **density**. By a series of experiments it has been found that **the density of all elementary gases is equal to their atomic weights.** One gramme of hydrogen weighed at 0° C. and 760 mm. barometrical pressure, occupies a space of 11·2 litres, and if we empty out the hydrogen and substitute oxygen, we find that the same bulk weighs 16 grammes, if nitrogen, 14 grammes, and if chlorine, 35·5 grammes; therefore we establish the rule that *the atomic weight of any elementary gas, weighed in grammes, always occupies* 11·2 *litres.* Turning to **compound** gases, we discover that **their density, referred to hydrogen, is equal to exactly half their molecular weight;** accordingly, we conclude that the molecule of a compound gas occupies a space exactly double that filled by an atom of hydrogen. If we weigh out 36·5 grammes of hydrochloric acid (H = 1 + Cl = 35·5) we find that it fills a space of 22·4 litres, and extending the experiments to other compound vapours we ascertain that the results agree, and that *the molecular weight of any compound gas, weighed in grammes, always occupies* 22·4 *litres.* It is evident, therefore, that no matter how complicated a molecule may be, it is only equal in volume to two atoms, and its whole bulk is *exactly twice the volume of any one atom of the constituent elements used in its production.* A glance at the following table will explain this, and in order that the meaning may be perfectly clear we have adopted the familiar volume of one gallon:—

1 gallon	H	and	1 gallon	Cl	= 2 gallons	HCl	(hydrochloric acid).
2 ,,	H	,,	1 ,,	O	= 2 ,,	H_2O	(steam).
3 ,,	H	,,	1 ,,	N	= 2 ,,	NH_3	(ammonia).

But we rarely meet with a general rule which is universally applicable; therefore it is not astonishing to find several exceptions to the axioms just propounded. It has been proved by experiment that the densities of the vapours of phosphorus and arsenic, instead of coinciding with their atomic weight, are double, so it follows that the atoms composing such fumes only occupy half the volume of an atom of hydrogen. Instead of 31 grammes of phosphorus vapour occupying 11·2 litres, it requires 62 grammes to fill the space, and similarly, instead of 75 of arsenic, 150 are required. Thus:—

3 galls.	H	and	½ gall.	P	= 2 galls.	PH_3	(phosphuretted hydrogen).
3 ,,	H	,,	½ ,,	As	= 2 ,,	AsH_3	(arseniuretted ,,).

On the other hand, mercury and cadmium, when in vapour, are found to possess a density only half as great as their atomic weights; therefore 200 grammes of mercury vapour will occupy 22·4 litres instead of 11·2; and it follows that two volumes of mercuric chloride ($HgCl_2$) must contain two volumes of Hg and two volumes of Cl.

The complete law of the combination of elements in a gaseous state by volume is usually stated as follows:

The combining volumes of all elementary gases are equal, excepting those of phosphorus and arsenic, which are only half the others; and those of mercury and cadmium, which are double those of the other elements.

There are several compounds which do not appear to follow the law of their molecules in a state of vapour, each being equal in volume to two atoms. This is accounted for by the explanation that it is impossible to take their correct densities as regards hydrogen, as they evidently undergo some change, denominated *dissociation*, when a sufficiently high temperature is applied in order to obtain them in the gaseous condition. Ammonium chloride, for instance, which is one of these exceptional bodies, appears to become dissociated into hydrochloric acid and ammonia gases when heated to the state of vapour; but again reunites and returns to its original partnership whenever the temperature is permitted to fall.

IV. ATOMICITY.

On glancing at the table of combination by volume just given, it is noticeable that while 1 atom of H combines with one atom of Cl to produce a molecule of HCl, yet that 1 atom of O requires 2 atoms of H to form 1 molecule of H_2O. In this latter case it is evident that a condensation takes place, and that the atom of oxygen possesses the power of fixing and saturating, as it were, 2 atoms of hydrogen. Here, therefore, we discover a relation between atoms totally distinct from their atomic weights. The following table exhibits this new relation :—

1	molecule	HCl	contains	1	atom of	H	and	1	atom of	Cl.
1	„	H_2O	„	2	„	H	„	1	„	O.
1	„	NH_3	„	3	„	H	„	1	„	N.
1	„	CH_4 (Marsh Gas.)	„	4	„	H	„	1	„	C.

This relation of bodies to each other in atom fixing power is called **atomicity**, and occasionally **quantivalence.** Atomicity, therefore, may be described as the measure of the power which one atom possesses of invariably attracting to itself a given number of other atoms. It is the value or, as it were, the capacity for saturation, which atoms bear to each other. This value, which must be kept totally distinct in the student's mind from the idea of atomic weight, is, however, like the latter, referred to hydrogen as unity. Atoms which are capable of fixing only 1 atom of hydrogen to form a stable compound, are called **monads,** like *chlorine;* those which, like oxygen,

can always fix	**2**	atoms of a monad	are called	**dyads**;	those that
can fix . .	**3**	„	„	**triads**;	„
„ . .	**4**	„	„	**tetrads**;	„
„ . .	**5**	„	„	**pentads**;	„
„ . .	**6**	„	„	**hexads.**	

The atomicity of bodies is represented by small ticks and Roman figures placed over the symbol, as follows :—

Monad	H'
Dyad	O''
Triad	Bi'''
Tetrad	C^{iv}
Pentad	P^{v}
Hexad	S^{vi}

V. GRAPHIC FORMULÆ AS EXPONENTS OF THE DOCTRINE OF ATOMICITY.

In order to render the theory of atomicity easy of comprehension, it has been assumed that atoms possess a certain number of points of saturation, which must be joined to other atoms before a stable molecule can be produced, capable of existence in a free state. It is sometimes customary to represent this junction by hieroglyphics, called **graphic formulæ,** in which the symbols of the atoms are represented as being united to each other by certain lines equalling in number the bonds of union they are supposed to possess. In using such formulæ, care must be taken to distinguish between the theoretical and the actual; the diagrams are intended **for purposes of explanation only, and they cannot be held as actual representations of the real constitution of the molecules they illustrate.** For example :—If the atom of

hydrogen, which is a monad, be represented by H, then hydrogen in the free state is produced by a saturation of the bond of union by another atom of H; consequently a molecule of free hydrogen is graphically portrayed thus, H—H. Following up this system, the molecules represented in the last table of examples are graphically formulated as follows:—

1 molecule of hydrochloric acid } HCl. 1 molecule of steam } H_2O. 1 molecule of marsh gas } CH_4.

H—Cl. H—O—H

```
   H
   |
H—C—H
   |
   H
```

In the same manner in which two atoms of hydrogen unite to form a molecule, may the atomicity of other atoms be modified by self saturation. Thus, carbon which is represented above as exhibiting its full atomicity in CH_4, may form an almost illimitable series of compounds with hydrogen by self saturation of one or more of its bonds of union with other carbon atoms, thus:

Methyl hydride.

```
   H
   |
H—C—H
   |
   H
```

or CH_4.

Ethyl hydride.

```
   H  H
   |  |
H—C—C—H
   |  |
   H  H
```

or C_2H_6.

Propyl hydride.

```
   H  H  H
   |  |  |
H—C—C—C—H
   |  |  |
   H  H  H
```

or C_3H_8

Many elements, in this manner, form various series of compounds in which they exhibit totally different atomicities. Among these ought to be specially mentioned nitrogen, phosphorus, arsenic, antimony, and bismuth. Those atoms which are truly pentad, possessing the power of fixing five atoms of a monad, may become triad by the self saturation of two of their bonds. For example:—Nitrogen forms a compound, called ammonia, which can exist at liberty, but should it be brought into contact with hydrochloric acid, the two self saturating bonds will at once unite with the elements of the acid, when a new and more stable compound, named ammonium chloride, will be formed, in which the nitrogen will exhibit its full pentad atomicity, thus:—

Ammonia, NH_3.

```
   H
   |
H—N—H
   \/
```

Ammonium Chloride, NH_4Cl.

```
  H  H
   \/
H—N—H
   |
   Cl.
```

Many metals likewise exhibit this property in a marked degree. For instance, mercury is in its fullest state a dyad, Hg″, but by two atoms self-saturating each other at one bond, a combination Hg_2 is produced, which also acts as a dyad. The first forms a class of salts called *mercuric*, and the second gives birth to *mercurous* compounds. Their respective chlorides may be thus represented:

Mercuric chloride, $Hg''Cl_2'$
Cl—Hg—Cl.

Mercurous chloride, Hg_2Cl_2.
Cl—Hg—Hg—Cl.

When a metal behaves in this manner, the terminations *ic* and *ous* are adopted: the former to distinguish the compounds in which the fullest atomicity is

exhibited, and the latter to mark the partially self-saturated salts. Thus we have cuprous and cupric, stannous and stannic, ferrous and ferric compounds, each class owning conspicuous reactions which enable us to discern between the two states of the same metal.

VI. RADICALS, ACIDS, AND BASES.

When a molecule is not fully saturated in all its atomicities, it cannot exist in the free state, except by union with another molecule of itself. Such unsaturated molecules may, however, be transferred from one compound to another without decomposition, and are then named **Radicals.** The atomicity of radicals is always equal to the amount of unsaturated bonds which they possess. For example, CH_4 (marsh gas) is a fully saturated compound, $\begin{array}{c} H \\ | \\ H\text{—}C\text{—}H \\ | \\ H \end{array}$ which, although it can exist in the free state, cannot combine with any more atoms. On the other hand, the radical CH_3 (methyl) has one bond unsaturated, $\begin{array}{c} H \\ | \\ H\text{—}C\text{—} \\ | \\ H \end{array}$, and it cannot of itself become free, but it can combine with other elements or radicals, behaving as a monad; and thus its chloride is CH_3Cl, or graphically $\begin{array}{c} H \\ | \\ H\text{—}C\text{—}Cl \\ | \\ H \end{array}$. A radical is, therefore, an unsaturated compound which can enter into combination and be transferred from one compound to another without decomposition, exactly like an element. Many chemists prefer to use the word **radical** for all bodies which behave as elements, the latter being called **simple radicals,** and the unsaturated groups of atoms, **compound radicals.** When radicals are examined, they are discovered to be in opposite states as regards electricity, some being electro-negative, and others electro-positive. In forming compounds, it is but rarely that the two radicals in the compound are in the same electric condition; as a rule, a compound body is composed of an electro-positive and an electro-negative radical, thus restoring the balance of electrical force in the new substance formed.

Before further developing the theory of atomicity of radicals, it is necessary that the definition of certain familiar chemical expressions be laid down and clearly understood.

1. **An Acid** is a compound of an electro-negative radical with hydrogen, which hydrogen it can part with in exchange for a metal or basylous radical. This hydrogen is called the "*replaceable hydrogen.*"
2. **An Acidulous Radical** is an element, or unsaturated group of elements, possessing electro-negative properties, and capable of combining with hydrogen to form an acid or with a basylous radical to form a salt.
3. **A Basylous Radical** is a metal or unsaturated group of elements possessing electro-positive properties, and capable of displacing the replaceable hydrogen of an acid to produce a salt.

VII. SALTS, AND THEIR MODE OF FORMULATION, AS BASED ON A KNOWLEDGE OF ATOMICITY.

A salt is the result of the displacement of hydrogen from an acid by a basylous radical and is therefore composed of an electro-negative and an electro-positive radical, in union with each other. All acids are capable of giving birth to a long series of salts by the displacement of their hydrogen by various basylous radicals; but it is a matter of indifference which of the latter performs this function, the acidulous radical remains unchanged as the *type* by which such class of salts are always characterized. Take, for example, **hydrochloric acid** (HCl). This is proved to be an acid, because by presenting a metal to it we can displace the H, and form a metallic chloride, such as **potassium chloride** (KCl). This chloride is the result of such displacement, and is a salt containing the basylous radical K in union with the acidulous radical Cl. We may displace the K by any other basylous radical, and form a chloride of the new radical, but the Cl remains through all chlorides as the unchangeable portion without which chloride cannot exist. Again, $(SO_4)''$ is an unsaturated group which acts as a dyad, and which, combined with two atoms of monad hydrogen, forms **sulphuric acid,** $H_2(SO_4)''$. The hydrogen may be displaced with any basylous radical, forming a class of salts called **sulphates.** We can thus have **potassium sulphate** $K_2'(SO_4)''$, or **sodium sulphate** $Na_2'(SO_4)''$; but the (SO_4) never varies, and is the indestructible group without which no sulphate can exist. It will be seen, therefore, that it is of the utmost importance to become familiar with the names, formulæ, and atomicities of the commoner radicals, both basylous and acidulous. The following tables are subjoined, and ought to be thoroughly committed to memory.

Table of the Active Atomicities of the Chief Basylous Radicals.

ELECTRO-POSITIVE.

MONADS.		DYADS (*continued*).	
NAME	FORMULÆ.	NAME	FORMULÆ.
Hydrogen	H.	Mercury (mercuric)	Hg
Potassium	K.	,, (mercurous)	(Hg_2).
Sodium	Na.	Tin (stannous)	Sn.
Lithium	Li.	Cerium (cerous)	Ce
Silver	Ag.	Iron (ferrous)	Fe.
Ammonium	(NH_4).	Cobalt (cobaltous)	Co.
Methyl	(CH_3).	Nickel (nickelous)	Ni.
Ethyl	(C_2H_5).	TRIADS.	
Amyl	(C_5H_{11}).	Gold (auric)	Au.
Phenyl	(C_6H_5).	Antimony (antimonious)	Sb.
DYADS		Bismuth (bismuthous)	Bi.
Calcium	Ca.	Glyceryl	(C_3H_5).
Barium	Ba.	TETRADS	
Lead	Pb.	Tin (stannic)	Sn.
Zinc	Zn.	Platinum	Pt.
Magnesium	Mg.	HEXADS.	
Cadmium	Cd.	Iron (ferric)	(Fe_2).
Copper (cupric)	Cu.	Aluminium (aluminic)	(Al_2).
,, (cuprous)	(Cu_2).	Chromium (chromic)	(Cr_2).

Table of the Active Atomicities of the commoner Electro-negative or Acidulous Radicals.

MONADS.

NAME.	FORMULÆ.
Hydrides	H.
Hydrates	HO.
Chlorides	Cl.
Hypochlorites	ClO.
Chlorates	ClO_3.
Iodides	I.
Iodates	IO_3.
Bromides	Br.
Bromates	BrO_3.
Fluorides	F.
Nitrates	NO_3.
Nitrites	NO_2.
Cyanides	CN *or* Cy.
Acetates	$C_2H_3O_2$.
Valerianates	$C_5H_9O_2$.
Sulphocyanides	CNS.
Hypophosphites	PH_2O_2.
Metaphosphates	PO_3.
Benzoates	$C_7H_5O_2$.
Cyanates	CNO.
Formates	CHO_2.
Oleates	$C_{18}H_{33}O_2$.

DYADS.

Oxides	O.
Sulphides	S.

DYADS (*continued*).

NAME.	FORMULÆ.
Sulphites	SO_3.
Thiosulphates (*or hyposulphites*)	S_2O_3.
Sulphates	SO_4.
Carbonates	CO_3.
Oxalates	C_2O_4.
Tartrates	$C_4H_4O_6$.
Lactates	$C_3H_5O_3$.
Succinates	$C_4H_4O_4$.

TRIADS.

Phosphates	PO_4.
Arseniates	AsO_4.
Citrates	$C_6H_5O_7$.
Malates	$C_4H_4O_5$.
Meconates	C_7HO_7.

TETRADS.

Ferrocyanides	FeC_6N_6 *or* $FeCy_6$.
Silicates	SiO_4.
Pyroarseniates	As_2O_7.

HEXAD.

Ferricyanides	$Fe_2C_{12}N_{12}$ *or* Fe_2Cy_{12}.

Let us illustrate the mode of using the foregoing tables in order to arrive at the formulæ of any known compounds:

It is desired to write **potassium iodide.** Potassium is K, and is a monad; the radical of iodides is I, which is also a monad: therefore **potassium iodide** must be $K'I'$, the two radicals combining in the simplest relation, one with one.

Plumbic iodide is now required to be written. Lead, Pb, in plumbic salts is a dyad; iodide, I, is a monad: therefore, the latter must be multiplied by two to make it balance the former, so the formula of the salt is $Pb''I_2'$.

Here the student must recollect that in chemical notation *all simple radicals, such as I, are multiplied by small figures placed immediately after and under the line of the symbol*, as in the formula just depicted. *Compound radicals*, on the other hand, *are multiplied by placing large figures before them.* Thus, suppose we wish to indicate two molecules of the radical of nitrates; we write $2NO_3$. It would not be correct to write N_2O_6, because the instant the formula NO_3 is altered, it no longer represents a nitrate. Compound radicals, therefore, must not have their small figures changed, but must invariably be multiplied by the large figures placed on the left; and in cases where the formula is long, a pair of brackets is also desirable, thus—$Pb''2(C_2H_3O_2)'$. As an example we shall take the series of sulphates:—The radical SO_4 being a dyad, the formulæ of its compounds, first with a monad radical, such as potassium, secondly with a dyad radical like calcium, and thirdly with a h[illegible], ferric iron, will be as follows:—

Potassium sulphate . . .	$K_2{}'(SO_4)''$.
Calcium sulphate	$Ca''(SO_4)''$.
Ferric sulphate	$Fe_2{}'''3(SO_4)''$.

In the **ferric sulphate** we have a balance of value similar to that produced by two threepenny pieces on the one hand, and three sets of twopences on the other. One more example will suffice. The radical of **phosphates** is $(PO_4)'''$. **Phosphoric acid** (the radical combined with hydrogen) will therefore be $H_3{}'(PO_4)'''$. Just as three pennies are equal in value to one threepenny-piece.

Calcium phosphate will present at first sight a greater difficulty, because, the calcium being a dyad, the question arises, How are two and three to be multiplied so as to be equal in value? By considering this substance as money, the problem may easily be solved. Each $(PO_4)'''$ represents a threepenny piece, and each Ca'' may stand for twopence; so, as two threepenny-pieces will balance three sets of twopence, giving an equal value of sixpence, the formula will be three of Ca'' and two of $(PO_4)'''$. The Ca'' being a simple radical, is multiplied by a small figure, and the $(PO_4)'''$, being compound, is multiplied by a large figure, making the formula of **calcium phosphate** $Ca_3{}''2(PO_4)'''$.

In chemical nomenclature a salt ending in *ide*, is produced by the union of a simple acidulous radical with a base, as iodine, I, **potassium iodide,** $K'I$. A salt ending in *ite*, is derived by displacement of hydrogen from an acid ending in *ous*, as **sulphurous acid** $H_2{}'(SO_3)''$, **potassium sulphite** $K_2{}'(SO_3)''$.

A salt ending in *ate* is obtained from an acid having a compound acidulous radical, the name of which ends in *ic*, as **sulphuric acid** $H_2{}'(SO_4)''$, **potassium sulphate** $K_2{}'(SO_4)''$.

When the atomicities of the acidulous radical are fully saturated by a base, the result is a *neutral salt*, as $K'I$, $K_2{}'(SO_4)''$, $Ca_3{}''2(PO_4)'''$. But when an acidulous radical combines with a basylous one of a lower atomicity, the hydrogen may only be partially replaced by the base, such an event signalizes the production of what is named an *acid salt*, as $K'H'(SO_4)''$ (**acid potassium sulphate**), $Ca''H_4{}'2(PO_4)'''$ (**acid calcium phosphate**). Another peculiar class of salts may be formed by the displacement of part of the acid radical by oxygen. Such salts are called *oxy* salts, sometimes *basic* salts. As an instance take **bismuth nitrate**. Bismuth being a triad requires three molecules of the monad nitrate, and the formula is therefore $Bi'''3(NO_3)'$; but two of the monad $(NO_3)'$ may be displaced by the dyad oxygen, and we have thus the formula $Bi'''O''(NO_3)'$ (**bismuth oxynitrate**). Many of the peculiar salts thus formed are termed, although incorrectly, *sub* in the British Pharmacopœia; thus, bismuth oxynitrate is called *bismuthi subnitras*.

VIII. SUMMARY OF THEORIES.

I. **An element** is a substance which cannot be analyzed. It is represented by a **symbol**, which in its turn indicates, when written (α') **one atom** of the element, (β') **one atomic weight,** which is the invariable quantity in which it combines with other substances by weight; (γ') the **atomicity** or combining value of the atom with other atoms; (δ') **a volume** in the gaseous state equal **to a single volume of hydrogen**.

II. A **compound** or an element in the free state is produced by the union of at least two atoms. It is represented by a **formula** which signifies (α') **one molecule** of the compound, (β') **one molecular weight,** equalling the sum of the atomic weights of the elements of which it is composed; (γ') **its atomicity,**

or combining value as regards other substances; (γ) a **volume in the gaseous state equalling two volumes of hydrogen.**

IX. EMPIRICAL, MOLECULAR, and RATIONAL or CONSTITUTIONAL FORMULÆ.

The union of symbols to express the constitution of a compound body is called a **formula.** Of such means of expression we have three varieties: (1) The **empirical formula,** merely giving the simplest possible expression of the ratio in which the elements are combined in the compound. (2) The **molecular formula,** giving the actual number of atoms supposed to be contained in each molecule of the substance, as distinguished from the mere numerical ratio. (3) The **rational** *or* **constitutional formula,** which goes still further and professes to show how the atoms are really arranged, according to the theory accepted and desired to be demonstrated. Examples of these three varieties may be found in the case of acetic acid; viz:—

CH_2O. *Empirical formula* (simplest relation of the atoms only).

$C_2H_4O_2$. *Molecular formula* (true number of atoms in each molecule).

$HC_2H_3O_2$.
C_2H_3OHO.
CH_3COHO. } *Rational* or *constitutional formulæ* (the first showing it to be an acid with H displaceable; the second, that it is the hydrate of a radical acetyl; and the third indicating the separation of CH_3 by the action of electricity.

Empirical formulæ are deduced from the percentage composition of the substance, found on analysis by (1) dividing the percentage of each element by its own atomic weight; (2) taking the lowest of these results as unity and dividing all the other quotients by it.

For example, acetic acid shows on analysis,—

Carbon	40·00
Hydrogen	6·66
Oxygen	53·34
	100·00

Dividing as above directed, we have,—

$$40{\cdot}00 \div 12 = 3{\cdot}33 \text{ carbon}$$
$$6{\cdot}66 \div 1 = 6{\cdot}66 \text{ hydrogen}$$
$$53{\cdot}34 \div 16 = 3{\cdot}33 \text{ oxygen.}$$

Taking now carbon as unity and writing it C, we have,—

$$H\,(6{\cdot}66) \div C\,(3{\cdot}33) = H_2$$
$$O\,(3{\cdot}33) \div C\,(3{\cdot}33) = O,$$

and the formula is therefore CH_2O.

Again, take the case of ferric oxide, which contains—

Iron	70·00
Oxygen	30·00
	100·00

Dividing as before by the atomic weight, we have,—

$$70 \div 56 = 1{\cdot}25 \text{ iron.}$$
$$30 \div 16 = 1{\cdot}875 \text{ oxygen.}$$

Taking now the lower number as unity, we have,—

$$O(1{\cdot}875) \div Fe\,(1{\cdot}25) = 1{\cdot}5\ O.$$

But as half, or any fraction, of an atom cannot exist, therefore $FeO_{1.5}$ is impossible. Hence we multiply both elements by 2, thus getting Fe_2O_3, which is the simplest possible relation in whole numbers, and therefore the correct empirical formula.

Molecular formulæ are obtained by submitting the results of the calculation of the empirical formulæ to the tests of either density or atomicity. *If the substance be volatile we take its vapour density* (*see* **Vapour Density** in **Author's Analytical Chemistry**, chapter i. section 13), and by the rule that *all compounds in a state of vapour have a density equal to half their molecular weight*, we obtain the true formula. For example, we have already found the empirical formula of acetic acid to be CH_2O, giving a molecular weight of 30; thus,—

$$\begin{aligned} C &= 12 \\ H_2 &= 2 \\ O &= 16 \\ & \underline{\underline{30}} \end{aligned}$$

But on taking the vapour density we find that the weight of a given volume of acetic acid vapour divided by that of an equal volume of hydrogen is 30, so that we see that the true molecular weight of the acid must be 60, or just double, and the true molecular formula is then—

$$\begin{aligned} C_2 &= 24 \\ H_4 &= 4 \\ O_2 &= 32 \\ & \underline{60} \end{aligned}$$

If, however, the compound be *not volatile*, or should it suffer dissociation when heated, we cannot get at its vapour density; but we must determine its molecular formula *by combining it with some body of which we already know the true combining weight and atomicity*. For the sake of making this clear we will still take the same example, namely, acetic acid, although it would, being volatile, not really require this process except as a confirmation. Suppose, therefore, the taking of the density to be for some reason inconvenient, we should make some pure and dry argentic acetate. Of this compound we should weigh out a certain quantity, say one gramme, and submit it to ignition, thus driving off the acetic radical, and leaving ·6468 gramme of metallic silver. Having now proved that one gramme of argentic acetate contains ·6468 gramme of silver, the balance of ·3532 gramme must represent the weight of the acetic radical. By simple proportion we next inquire, If ·6468 gramme of silver combined with ·3532 gramme of acetic radical, how much of the latter would be required to combine with an atomic weight of silver taken in grammes (108)? thus,—

$$\cdot 6468 : \cdot 3532 :: 108.$$
$$\frac{\cdot 3532 \times 108}{\cdot 6468} = 58 \cdot 98.$$

But now atomicity steps in and says that silver is a monad and must therefore have displaced an atom of H from the acid in forming the salt, so it is clear that the atomic weight of H = 1 must be added to the above, giving us 59·98. Knowing, from the atomic weights of C, H, and O, that we must neglect the fraction, we have 60 for the nearest whole number, thus once more confirming the idea that the true molecular formula of acetic acid is $C_2H_4O_2 = 60$, and not $CH_2O = 30$, as found for the simple empirical formula.

X. CHEMICAL EQUATIONS.

The mode in which bodies react upon each other is represented by a series of letters, numerals, and signs, called a **chemical equation.** In such diagrams the ordinary signs of arithmetic are used, such as + (plus) added to, − (minus) deducted from, = equals. As the thorough understanding of a chemical equation is of the utmost consequence, we shall trace the idea from its simplest form. Let us say that 2 equals 2, a fact comprehensible by the most ordinary uneducated intellect; yet although it be an equation, it conveys little instruction even when symbolised chemically: thus, $H_2 = H_2$ represents no chemical action, and we have already learned that the delineation of such action, which produces complete changes in the bodies acted upon, is one of the essences of the science of Chemistry. If, however, we say that 2 added to 1 equals 3 ($2 + 1 = 3$), we look upon an equation which teaches and suggests something for the due appreciation of which a certain amount of education is required. An untutored savage knows intuitively that two stones he may pick up equal in number any other two: but some education must evidently be required ere he can confidently assert that one stone added to two stones will show a result of three. Reducing this to a chemical equation, we have

$$H_2 + O = H_2O.$$

Here then is a true example of what we mean, because it teaches something; the individual atoms on either side of the sign balance each other in point of numbers, and a totally new substance is produced from the ingredients employed. These are the essential characteristics of a true chemical equation. An equation in which two substances unite to produce a third body is said to represent a **single decomposition.** Such an equation may be reversed, when it will indicate the splitting up of a body into two different products, but still the action portrayed is that of a single decomposition. Thus, **potassium chlorate,** on being heated, yields **potassium chloride** and **oxygen,** which reaction would be represented as follows :—

$$KClO_3 = KCl + O_3:$$

a correct equation, exhibiting all the essential points already mentioned. (1) It teaches the fact that oxygen and potassium chloride *can* be produced from potassium chlorate; (2) the same number of atoms of K, Cl, and O, respectively, are found on each side of the equation; (3) from the substance operated upon, two entirely different bodies have been produced. Of this simple form of equation there are necessarily very few, the more usual specimens being those of **double decomposition.** By this we mean the production of at least two distinct bodies from the reaction upon one another of an original two. Take, for example, the reaction of **potassium iodide** on **mercuric chloride** (already referred to when chemical action was under consideration), which exhibits a type of a vast number of equations representing actions wherein the acidulous radicals of the substances employed merely interchange their base. From **mercuric chloride** and **potassium iodide** we produce **mercuric iodide and potassium chloride,** which is thus represented as an equation :—

$$Hg''Cl_2' + 2K'I' = Hg''I_2' + 2K'Cl'.$$

W... ...ce the large figure 2 before the KI and the KCl, in order to show ...se two molecules of the former, and produce two molecules of the ...hat this must be so becomes evident from the fact that Hg, as a ...ires two atoms of monad iodide; and there being only one I in each ...f KI, two molecules must be employed to yield the I_2 demanded. ...uation the mercuric chloride and potassium iodide are called the ...; the mercuric iodide, the **chief product**; and the potassium

chloride, the **bye-product.** In equations these bye-products are often a source of considerable difficulty, especially when they happen to be numerous, and the equation does not represent a simple interchange like the one just considered; but a knowledge of the bye-products of any particular action is only to be acquired from a study of the chief elements and their compounds. Such a study may, however, be greatly facilitated by committing to memory examples of a series of familiar actions, and establishing in the mind a set of typical equations. In this we shall endeavour to assist the learner by noting some examples of some of the most common chemical actions *seriatim*:—

1. When a metal dissolves in **hydrochloric acid**, a **chloride** of the metal is produced and **free hydrogen** is evolved. Take for example the manufacture of **zinc chloride**: Zn being a dyad will require two atoms of Cl to form the chloride, and as each molecule of **hydrochloric acid** only contains one atom of Cl, we shall require to use two molecules of the acid, and the equation will be:—

$$Zn'' + 2H'Cl' = Zn''Cl_2' + H_2'.$$

Applying the same rule to iron, we have—

$$Fe'' + 2H'Cl' = Fe''Cl_2' + H_2'.$$

2. When a metal which is soluble in **diluted sulphuric acid** dissolves in that fluid, a **sulphate** of that metal is produced, and free **hydrogen** gas evolved. In this case the sulphate being a dyad, as well as the metals which we find behaving in this way in Pharmacy, one of each only is required, and the action is usually represented as a simple displacement of the hydrogen of the acid by the metal. Thus with zinc and iron respectively, we have—

$$Zn'' + H_2'(SO_4)'' = Zn''(SO_4)'' + H_2'.$$
$$Fe'' + H_2'(SO_4)'' = Fe''(SO_4)'' + H_2'.$$

3. When an *acid* acts upon a **carbonate**, a *salt* is produced by the union of the **metal** *of the carbonate* with the **acidulous radical** *of the acid employed*, and **carbonic anhydride**, CO_2 (commonly called carbonic acid gas) and **water** (H_2O) are produced. Thus **calcium carbonate** dissolves in **hydrochloric acid** to produce **calcium chloride**, and **carbonic anhydride** is evolved with effervescence and water formed, thus:—

$$Ca''(CO_3)'' + 2H'Cl' = Ca''Cl_2' + CO_2 + H_2O.$$

The CO_3, being an unsaturated radical, cannot exist at liberty, and it therefore gives up one atom of oxygen to two atoms of hydrogen from the acid, forming water and leaving CO_2, which, being a fully saturated molecule, comes off in the free state. Two molecules of HCl are required to yield the two Cls necessary for the formation of the calcium chloride. Extending this principle to other actions, we have **magnesium carbonate** dissolving in **sulphuric acid and yielding magnesium sulphate.**

$$Mg''(CO_3)'' + H_2'(SO_4)'' = Mg''(SO_4)'' + CO_2 + H_2O.$$

The sulphate radical being a dyad as well as the magnesium, we only require one molecule of each. Again, **potassium carbonate** and **acetic acid** yield **potassium acetate**; thus:

$$K_2'(CO_3)'' + 2H'(C_2H_3O_2)' = 2K'(C_2H_3O_2)' + CO_2 + H_2O.$$

Here we have two atoms of monad K in the carbonate, which require two molecules of the monad acetate radical, and yield two molecules of the **potassium acetate, together with the usual bye-products.**

An equation of this class becomes more complicated when the action takes place between the carbonate of a dyad metal and an acid having a triad

radical. Thus, to form **calcium citrate** we require *three molecules* of **calcium carbonate,** and *two molecules* of **citric acid,** because the simplest way in which a dyad and a triad can be brought to balance each other is by multiplying the former by 3 and the latter by 2. When we thus employ three molecules of a carbonate, it is evident that we must produce three molecules of each of the bye-products, therefore the finished equation will be :—

$$3Ca''(CO_3)'' + 2H_3'(C_6H_5O_7)''' = Ca_3''2(C_6H_5O_7)''' + 3CO_2 + 3H_2O.$$

4. When some metals are heated with **strong sulphuric acid** they dissolve, forming a **sulphate,** evolve **sulphurous anhydride** (SO_2, commonly called sulphurous acid gas) and produce water. This reaction takes place at the expense of a molecule of H_2SO_4, which becomes divided into SO_2 and H_2O, thus leaving one atom of oxygen, which in its turn combines with the H_2 of a second molecule of sulphuric acid, and liberates the SO_4 to combine with the metal used. In such an equation, therefore, we must employ one of a dyad metal to two of sulphuric acid, forming a sulphate of the metal and the above-named bye-products. Examples are found in the equations for **cupric** and **mercuric sulphates** :—

$$Cu'' + 2H_2'(SO_4)'' = Cu''(SO_4)'' + SO_2 + 2H_2O.$$
$$Hg'' + 2H_2'(SO_4)'' = Hg''(SO_4)'' + SO_2 + 2H_2O.$$

5. When a metal dissolves in slightly diluted **nitric acid,** a **nitrate** is produced, and two molecules of **nitric oxide** gas (2NO) are usually evolved and water formed. The nitric oxide gas is produced at the expense of 2 molecules of HNO_3, which become broken up into 2NO and H_2O, thus leaving three atoms of oxygen, which combine with the hydrogen of 6 other molecules of nitric acid to form 3 more molecules of water, thus liberating 6 molecules of NO_3 to combine with an equivalent quantity of the metal, and the total bye-products of this reaction are, therefore, $2NO + 4H_2O$. Consequently it is clear that in all such equations we must use 8 molecules of HNO_3 and enough metal to combine with $6NO_3$ out of the 8, according to the atomicity of the metal, producing as many molecules of the nitrate as we use atoms of the metal. Thus with a *monad* metal like **silver,** a *dyad* like **mercury,** and a *triad* like **bismuth,** we have respectively the following **equations** :—

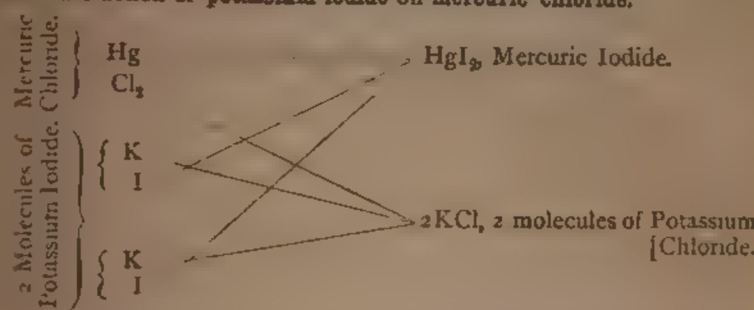
$$Ag_6' + 8H'(NO_3)' = 6Ag'(NO_3)' + 2NO + 4H_2O.$$
$$Hg_3'' + 8H'(NO_3)' = 3Hg''2(NO_3)' + 2NO + 4H_2O.$$
$$Bi_2''' + 8H'(NO_3)' = 2Bi'''3(NO_3)' + 2NO + 4H_2O.$$

Such are a few typical equations, and it is to be hoped that their careful study, conjoined with a return to their consideration when the facts involved are more prominently brought forward, will smooth the way towards, and lighten the task of acquiring, this all-important section of Chemistry. The student is therefore earnestly urged to learn equations (not merely by heart in order to pass the ordeal of an examination), but to search out the reasons involved, so that he may retain, and be able to use, the whole of his chemical knowledge through life. The theories of atomicity and equations ought to be so thoroughly mastered that the young pharmacist may, without a moment's hesitation, write down the formula representing any ordinary reaction without reference to any chemical work.

In former times chemical reactions were represented by what was called a *diagram*. This was a series of lines drawn from one element to another to show that they combined in a particular manner. The following examples of diagrams will explain themselves. They were very useful things in the hands of a teacher, but are now considered obsolete.

Diagram showing the result of heating **potassium chlorate** to be the formation of **potassium chloride** and **oxygen.**

Diagram of the action of **potassium iodide on mercuric chloride.**



XI. PRACTICAL APPLICATION OF EQUATIONS TO THE CALCULATION OF QUANTITIES BY WEIGHT AND BY VOLUME.

The equation is the starting-point, from which all calculations of the quantity of any substance required to perform a given decomposition, are determined. The two ideas must, however, be kept quite distinct.

1. **Calculations by Weight** are made by reducing the equations to figures, and then intelligently applying the rule of three. For instance, taking the simple equation already given for the making of oxygen, let us inquire how much oxygen would be obtained by heating 100 grammes of Potassium Chlorate.

Reducing the equation to figures, we have :—

$$\left\{\begin{array}{l} K = 39 \\ Cl = 35{\cdot}5 \\ O_3 = 48 \end{array}\right. = \left\{\begin{array}{l} K = 39 \\ Cl = 35{\cdot}5 \end{array}\right. + O_3 = 48$$

$$\underline{\underline{122{\cdot}5}} = \underline{\underline{74{\cdot}5}} + \underline{\underline{48}}$$

That is, in theory, 122·5 parts by weight of $KClO_3$ would yield on heating 74·5 parts of KCl and 48 parts of oxygen. Ordinary simple rule of three would then enable us to inquire, If $KClO_3$ would yield in theory O_3, what would 100 grammes of potassium chlorate produce? Thus we have the proportion :—

$$KClO_3 : O_3 :: 100$$

or in figures, $122{\cdot}5 : 48 :: 100.$

Working this out, we find that :

$$\frac{48 \times 100}{122{\cdot}5} = 39{\cdot}18.$$

So from 100 grammes of $KClO_3$ we should get 39·18 grammes of oxygen.

To any one with the most elementary knowledge of the rule of three, such calculations are very simple, the whole thing turning on (1) a correct statement of the equation and an accurate reduction to its combining weights,

and (2) the consideration that in rule of three we always work *from the fact we know to that we want to know.* One more example will suffice.

Supposing we are required to convert four ounces of mercuric chloride into mercuric iodide by precipitation with potassium iodide. How much potassium iodide is necessary, and what weight of mercuric iodide ought we to get, provided the process be accurately conducted? By the equation:—

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

One molecule of mercuric chloride requires two molecules of potassium iodide to form one molecule of mercuric iodide. Having arrived at this fact, we next proceed to reduce the equation to molecular weight, thus:—

$$\begin{array}{ccccccc}
Hg = 200 & & K = 39 & & Hg = 200 & & K = 39 \\
Cl_2 = \underline{71} & & I = \underline{127} & & I_2 = \underline{254} & & Cl = \underline{35{\cdot}5} \\
 & & 166 & & & & 74{\cdot}5 \\
 & & \underline{2} & & & & \underline{2} \\
\underline{\underline{271}} & + & \underline{\underline{332}} & = & \underline{\underline{454}} & + & \underline{\underline{149}}
\end{array}$$

Therefore, 271 parts by weight of $HgCl_2$, mixed with 332 parts by weight of KI, will yield 454 parts by weight of HgI_2. By the rule of three we then calculate:—

As $HgCl_2$ is to $2KI$ so are 4 ounces to the amount of KI required, stated in ounces or figures:—

$$\begin{array}{l}
271 \;:\; 332 \;::\; 4 \\
 \underline{4} \\
271)1328(4{\cdot}9 \\
\underline{1084} \\
2440 \\
\underline{2439} \\
\underline{\underline{1}}
\end{array}$$

ounces is therefore the quantity of potassium iodide sought.

Again, as $HgCl_2$ is to HgI_2 so are 4 ounces to the amount of HgI_2 which should be produced, stated in ounces.

$$\begin{array}{l}
271 \;:\; 454 \;::\; 4 \\
 \underline{4} \\
271)1816(6{\cdot}7 \\
\underline{1626} \\
1900 \\
\underline{1897} \\
\underline{\underline{3}}
\end{array}$$

is the quantity of HgI_2 we ought to obtain.

By these calculations we learn, that having started with 4 ounces of $HgCl_2$, we must employ 4·9 ounces of KI; and our precipitate, when dried, ought to weigh 6·7 ounces. It being the practice in manufacturing to disregard minute fractions, the British Pharmacopœia instructs us to use 4 ounces of $HgCl_2$, and 5 ounces of KI, quantities which are based upon such calculations as the above.

As a useful check upon the cost of the manufacture of any particular chemical, similar calculations are invaluable; thus, at the present prices (Nov., 1878) of the above ingredients, their cost would be 5*s.* 5*d.*; but as the yield of red iodide of mercury would be nearly 6½ ounces, it follows that the actual cost when made would be 10*d.* per ounce, to which would require to be added the usual estimate for labour and the wear and tear of plant.

2. **Calculations by volume** are very much more simple, and it is only necessary to bear in mind that in the gaseous state all atoms are supposed to be equal in volume to H, and all molecules to H_2. If therefore, in an equation, a molecule produces a molecule, no alteration in bulk takes place; but if a molecule produces an atom or two molecules respectively, then the size is, in the first case, halved, and in the latter, doubled. For example, we know that—

$$H + Cl = HCl;$$

or, in other words,—

1 atom H + 1 atom Cl = 1 molecule HCl;

so—

1 gallon H + 1 gallon Cl = 2 gallons HCl,

or any other volume-measure that might be required, in the same proportion. Supposing, to make the question more complicated, we had to consider what would happen if we exploded 10 gallons of H and 15 gallons of Cl. It is clear that in this case the 10 gallons of H would combine with the same volume, viz., 10 gallons of Cl, to form 20 of HCl, while there would be 5 gallons of Cl left over untouched. In all the equations for gases throughout this work, the quantities by volume will be found attached, and the student is advised to look them over, and compare them with the above example.

3. **Calculations from weight to volume, and vice versa,** are based upon the two propositions already laid down, that 11·2 litres of an elementary gas, and 22·4 litres of a compound gas weigh respectively their atomic or molecular weights in grammes. Suppose we inquire what the 39·18 grammes of oxygen, already found in a former calculation, would measure. By proportion we have the statement: if 16 grammes of oxygen occupy 11·2 litres what would 39·18 grammes measure.

$$16 : 11{\cdot}2 :: 39{\cdot}18,$$

$$\text{or } \frac{11{\cdot}2 \times 39{\cdot}18}{16} = 27{\cdot}43 \text{ litres of oxygen.}$$

The weight of a litre of any gas may also be obtained by the use of the **crith**, or weight of a litre of hydrogen, which is ·0896 gramme. If this be multiplied by the *atomic weight* of any *elementary gas*, or *half the molecular weight* of any *compound gas*, the weight of a litre of the gas in question is obtained. The calculations are all supposed to be done on gases at normal temperature and pressure, and the present is a mere introductory sketch, full details of the influence of change of the conditions when measuring being given elsewhere. (*See* **Specific Gravity, Thermometer,** and **Barometer** *in the Author's* **Analytical Chemistry,** *pages* 9–17, *and* 3–6.)

CHAPTER III.

SIMPLE BASYLOUS RADICALS.
SOURCES, ISOLATION, AND CHARACTERS.

THE elements, or simple radicals, are divided into two classes: the **metallic elements**, and the **metalloids**. It may be remarked, at this point, that—

METALLOIDS	METALS
Are usually electro-negative in the compounds they form on uniting with metals or compound basylous radicals. This class includes:	Are usually electro-positive in the compounds which they form on uniting with metalloids, or compound acidulous radicals. The metals used in pharmacy are:—

Metalloids	Metals	Metals
Arsenic*	Aluminium	Lead
Boron	Antimony	Lithium
Bromine	Barium	Magnesium
Carbon	Bismuth	Manganese
Chlorine	Cadmium	Mercury
Fluorine	Calcium	Nickel
Iodine	Cerium	Platinum
Nitrogen	Chromium	Potassium
Oxygen	Cobalt	Silver
Phosphorus	Copper	Sodium
Silicon	Gold	Strontium
Sulphur	Hydrogen	Tin
Selenium	Iron	Zinc

Following out the principle of the distinction between basylous and acidulous radicals, it is first necessary to consider the former class. We will therefore take the simple basylous radicals or metals *seriatim*, with special reference to their sources, isolation, and analytical detection, afterwards treating of compound basylous radicals in a separate chapter, and finally devoting a special chapter to each of the metalloids and their compounds with basylous radicals and with each other.

All simple basylous radicals are solid, except mercury (and hydrogen, if regarded as a metal), and most solid metals possess the properties of:—

1. **Malleability**, the capability of being spread out into plates, or leaves, or foil, under mechanical force. Gold-leaf offers the most striking ex-

* Arsenic is a connecting link between metals and metalloids, possessing to some extent the properties of both. For good reasons, it is recommended that the pharmaceutical student should regard arsenic as a metalloid, although in practical analysis this substance is detected and separated among the metals. Bismuth and antimony own similar properties, but for convenience they are classed among the metals.

ample of the tenuity to which a highly malleable metal may be hammered; and silver, platinum, copper, and tin form illustrations of the delicate leaf or foil to which these metals may be rolled. But pressure or blows on any malleable metal increase the specific gravity, rendering it harder, and inducing a tendency to brittleness. Such a condition would obviously unfit many of our best known and most useful metals for the uses to which they are constantly applied in the arts. By the simple process of annealing, however, any malleable metal may regain its original condition, as it likewise recovers its former specific gravity. Heating the metal to redness away from contact with the air (if it will bear such a heat without fusion), then cooling gradually or rapidly, according to the degree of softness required, constitute the whole process of annealing.

2. **Ductility**, that tenacity or power of resisting separating force which is exemplified in the art of wire-drawing. This consists in drawing metallic rods through a succession of cone-shaped perforations in a steel plate, each hole being a shade smaller than its predecessor, until the desired degree of fineness has been obtained. Under such treatment, the metal is apt to become brittle, but is at once restored to its original condition, as in the analogous cases of metals being passed through rolling mills or under the hammer, by the process of annealing. It having been found necessary in the arts to determine the order of tenacity of ductile metals, this is accomplished by noting the amount of weight demanded in order to break wires which have been drawn through the same orifice. The order is as follows:—

Iron,	Gold,
Copper,	Zinc,
Platinum,	Tin,
Silver,	Lead.

3. **Fusibility**, the degree of susceptibility to the melting power of heat possessed by metals. This sensitiveness is exceedingly variable, and reaches from mercury, which is always fluid above $-39°$ Fahr., to cast iron, which requires $2786°$, not to mention platinum, which is only partly fusible by the oxyhydrogen blowpipe. Iron, platinum, and some other metals, possess an additional property when in a partially melted condition, which, in the arts, greatly enhances their value. Before fluidity supervenes, they acquire an adhesive or viscous state, which admirably suits them to endure the blows of the hammer or the pressure of the rolling-mill; to be puddled in the furnace, and welded together either in or out of it. It is this specialty which enables us to unite separate pieces of iron or steel without the aid of solder, and to hammer or compress spongy platinum into a solid bar.

Simple basylous radicals form two varieties of combinations:

1. Those with acidulous radicals, called **salts**, as already explained.
2. Those **alloys** which are produced by the mutual combination of metals themselves.

Although most metals may to some extent exist in a state of combination with each other (a state called alloy, and, when mercury is present, amalgam), yet the chemical affinity between them is often so feeble, and the restraint which binds them together so weak, that the synthesis is easily disturbed. But it has been observed that in proportion to the dissimilarity between the metals of an alloy or amalgam is the stability and permanence of the compound increased; and yet in no case does that peculiar alteration of physical character, which specially marks chemical combination, occur to any great

A metal alloyed or amalgamated with another metal, retains most distinguishing features, and no such metamorphosis or transmutation as we find in the combination of a metal with a gas, an acid, or an The alteration which usually occurs affects the metallic tenacity, colour, degree of hardness, although alloys of metals possessing wholly opposite chemical characteristics, are remarkable for their exceeding frailty of mutual cohesion.

Table of the Composition of the more Common Alloys.

Brass	$Cu(84{\cdot}3) + Zn(5{\cdot}2) + Sn(10{\cdot}6)$.
Britannia Metal	$Sn(25) + Sb(50) + Bi(25)$.
Bronze	$Cu(86) + Zn(11{\cdot}1) + Sn(2{\cdot}9)$.
Bell Metal ...	$Cu(80) + Zn(5{\cdot}6) + Sn(10{\cdot}1)$.
Gun Metal ...	$Cu(93) + Sn(7)$.
Pewter	$Sn(86) + Sb(14)$.
Speculum Metal	$Cu(50) + Zn(21) + Sn(29)$.
Solder (soft) ...	$Pb(1) + Sn(2)$.
” (hard) ...	$Cu(8) + Zn(8) + Sn(1)$.
Type Metal ...	$Pb(69) + Sb(15{\cdot}5) + Bi(15{\cdot}5)$.
White Metal ...	$Cu(7{\cdot}4) + Zn(7{\cdot}4) + Sn(28{\cdot}4) + Sb(56{\cdot}8)$.
Oreide	$Cu(73) + Zn(12{\cdot}3)$ [with $MgO(4{\cdot}4)NH_4Cl(2{\cdot}5)$ $KHC_4H_4O_6(6{\cdot}5)$ and $CaO(1{\cdot}3)$ as fluxes].

CLASS I. MONADS.

Among these are **potassium** and **sodium**, which are distinguished by the peculiarity of each metal forming but one chloride. Their carbonates are soluble in water. Heat fails to expel the water contained in their alkaline and caustic hydrates; they decompose water at all temperatures; energetically combine with oxygen; and they are soft, easily fusible, and volatile at high temperatures. **Silver** is only distantly related to the alkali-metals, as, for instance, in forming an alum, similar to that obtained from aluminium and potash. **Hydrogen**, although a gaseous body, and always formerly treated in chemical works as a metalloid, is, for various reasons to be given hereafter, considered by us a monad metal.

HYDROGEN (*Hydrogenium*). **Symbol, H.** *In the free state,* H_2. **Atomic Weight, 1. Atomicity, Monad. Density, 1. Weight of 1 litre,** *at* 0° C. *and* 760 *mm.*, **·0896** *gramme.* **One gramme,** *at* 0° C. *and* 760 *mm.*, **occupies 11·2 litres.**

This colourless, inodorous, and tasteless gas, is the lightest known body in nature; and, as being the standard adopted among scientific men (both as regards its combination by weight and volume) to which all other bodies are referred, and with which they are compared, it deservedly commands prior study.

By some chemists it has been described as a gaseous metal, under the names **hydrogenium** and **hydrium**, on account of alloys which have been apparently formed by it with **palladium** and other metals. This idea seems to have received confirmation from the fact that such metals, although known to have absorbed many hundred times their bulk of hydrogen, refused to part with any of it, either *in vacuo* or at a red heat. It is beyond doubt, also, that the chief relations of hydrogen are electro-positive; and, looked at in this light, we prefer to treat the body as if its metallic properties had been definitely proved.

Hydrogen was alluded to by Paracelsus as early as the 16th century, although first isolated by Cavendish in 1766; an honour which is likewise claimed for Watt and Lavoisier. It is found in the vapours which emanate from certain volcanic fissures in Iceland; it forms one-fourth of the compound called marsh-gas; water contains it to the extent of one-ninth; in smaller quantities it appears combined with numerous other substances; and it is present in all vegetable and animal organisms, and in many minerals. The lightest body known in nature (the oxygen of the air is sixteen times heavier), it might naturally be supposed that an inverted, open-mouthed jar would be in no danger of losing its contents. Yet the reverse is the truth, as we find that the law of diffusion, which is more or less characteristic of all gases, prompts the hydrogen in the jar to diffuse downwards, as well as in every other direction, so that in a very short period of time the vessel, once full of this gas, would be found occupied by ordinary atmospheric air. This law of diffusion, as already mentioned, proceeds in inverse proportion to the square root of the specific gravity of the gas.

Hydrogen may be prepared as follows:—

1. By throwing **potassium** on water, when **potassium hydrate** is simultaneously formed.

$$K_2 + 2H_2O = 2KHO + H_2.$$

This action is simply one of direct displacement, and is so violent that the heat produced inflames the hydrogen.

2. By passing the vapour of water over red-hot iron; forming **ferroso-ferric oxide**, and liberating **hydrogen**.

$$Fe_3 + 4H_2O = Fe_3O_4 + 4H_2.$$

3. By the action of dilute **sulphuric acid** or **hydrochloric acid** upon **iron** or granulated **zinc**, sulphates of the metals being formed in the first case, and chlorides in the second:—

$$Fe_2 + 2H_2SO_4 = 2FeSO_4 + 2H_2. \qquad Fe_2 + 4HCl = 2FeCl_2 + 2H_2.$$
$$Zn_2 + 2H_2SO_4 = 2ZnSO_4 + 2H_2. \qquad Zn_2 + 4HCl - 2ZnCl_2 + 2H_2.$$

Granulated zinc is the preferable form in which to use this metal for the evolution of hydrogen. It is thus made: The ordinary zinc of commerce, reduced to moderately small fragments, is fused in an iron ladle over a brisk fire. As soon as the metal has become fluid, it is poured into a bucket of cold water, from a height of about a dozen feet, when each drop expands into a trumpet-shaped mass, which, exposing a considerable surface to chemical action, is readily dissolved when in contact with a suitable acid.

4. By the action of **potassium** or **sodium hydrate** upon **zinc**, **aluminium**, or **tin**, forming *zincates*, *aluminates*, or *stannates*:—

$$Zn + 2KHO = K_2ZnO_2 + H_2.$$
$$2Al_2 + 6NaHO + 3H_2O = Na_6Al_4O_9 + 6H_2.$$

5. By the action of **potassium** or **sodium hydrate** upon **oxalates**, and upon many other organic salts:—

$$K_2C_2O_4 + 2KHO = 2K_2CO_3 + H_2.$$

Hydrogen is capable of liquefaction by submitting it to a pressure of 650 atmospheres in a tube cooled to - 220° Fahr. with the aid of solid carbonic anhydride. On suddenly releasing the pressure by opening a jet, the liquid hydrogen rushes out, forming a steel-blue spray of liquid, which solidifies

through the cold produced by its own evaporation, and falls as a hail of solid particles. This great discovery has been made by the aid of an ingenious apparatus devised by M. Pictet. The gas is but sparingly soluble in water or alcohol, one hundred gallons of either only dissolving or absorbing two gallons. It is condensed in the substance of several metals, notably **platinum** (to the extent of 3·8 volumes), **palladium** (376 volumes), and **iron** (about two volumes). The late Professor Graham, who studied this phenomenon carefully, applied the term **occlusion** to this singular state of absorption. During his researches it came to light that the meteoric iron of Lenarto, when placed in a good vacuum, yielded 2·85 times its volume of gas, consisting of 85·68 per cent. of hydrogen, 4·46 of carbon monoxide, and 9·86 of nitrogen. When we reflect that spectrum analysis proves that hydrogen constitutes the chief element in the atmosphere of many of the fixed stars, and then gaze upon the fragment of such an aërolite as that of Lenarto, we can appreciate the words of Professor Graham, when he says that "this meteorite may be looked upon as holding imprisoned within it, and bringing to us, the hydrogen of the stars."

When a light is applied to **hydrogen** gas, as it issues from a jet in contact with the atmosphere, it inflames, producing water; but although thus proved to be combustible, it is not a supporter of combustion. The flame produced possesses intense heating power, notwithstanding its feeble illuminating properties; and should a stream of **oxygen** gas be impinged upon it, so that neither jet occurs in excess, the oxyhydrogen blast resulting, yields, with the exception of that generated by an electric current, the most concentrated and irresistible heat with which we are yet acquainted. The absorption of gases by certain metals is strikingly exemplified by the following simple experiment:—If a fragment of spongy platinum be exposed to a jet of hydrogen, it "occludes" the gas so rapidly that sufficient heat is generated to produce final inflammation of the hydrogen. Seizing upon this circumstance enabled the inventor of the now almost obsolete hydrogen lamp to obtain an instantaneous light, long before lucifer matches had been popularized. The objection to this means of obtaining an immediate light lies in the fact that, if the hydrogen lamp is left unused, its little mass of spongy platinum becomes damp, through absorption of moisture from the air, so that its usefulness for a time is lost.

Free hydrogen is feeble in its action on other substances, but in the *nascent* condition it is remarkably powerful. It will be understood that by the term *nascent* is meant the instant of its liberation from any body with which it may happen to be combined. In order to obtain the full benefit of this peculiar activity it is only necessary to expose the matter to be decomposed, in a state of solution, to the action of a mixture of **zinc** and **sulphuric acid**, or some other similar combination of ingredients from which hydrogen may be evolved. By such exposure bodies are, in chemical language, said to be "reduced" from a higher to an inferior state of oxidation, on account of the abstraction of their oxygen to form water. For example:—**Ferric** salts are reduced to *ferrous*; or **nitric acid** to *ammonia*.

Hydrogen possesses the property of entering into combination with all the non-metallic elements as follows:—

NON-METALLIC COMPOUNDS OF HYDROGEN.

	ELEMENT.	SYMBOL.	RESULT OF COMBINATION.
Monads	Chlorine . .	HCl	Hydrochloric Acid.
	Bromine . .	HBr	Hydrobromic „
	Iodine . . .	HI	Hydriodic „
	Fluorine . .	HFl	Hydrofluoric „
Dyads	Oxygen . .	H_2O	Water.
	Sulphur . .	H_2S	Sulphuretted hydrogen.
	Selenium . .	H_2Se	Seleniuretted „
Triads	Nitrogen . .	NH_3	Ammonia.
	Phosphorus .	PH_3	Phosphuretted hydrogen.
	Arsenic . .	AsH_3	Arseniuretted „
	Antimony . .	SbH_3	Antimoniuretted „
Tetrad	Carbon . .	CH_4	Marsh gas, and a long series of bodies called hydrocarbons, of which this compound is the starting point.

Hydrogen also combines with many metals and organic radicals to form combinations called "**hydrides.**" But it should be recollected that the atom of this element found in the basylous parts of salts has quite a different duty to perform from that occupying the acidulous. It is the latter combination which yields the hydrides just referred to, whilst the basylous radical of acids is wholly due to the former. The only metallic hydride of interest to the pharmacist is **cuprous hydride**, Cu_2H_2. This is a yellow powder, when first obtained by precipitating **cupric sulphate** with **hypophosphorous acid,** but it quickly becomes reddish-brown. The precipitate occurs at about 160° F., but the product is decomposed if the heat be raised to 212°. It may be distinguished from metallic copper, to which it bears a great resemblance, by dissolving easily in dilute **hydrochloric acid** with effervescence, whilst copper does not give rise to any action whatever.

LITHIUM. Symbol, Li. Atomic Weight, 7. Specific Gravity, 0·59. Melting Point, 356° F.

Lithium is found as *lepidolite* or *petalite* (**aluminium** and **lithium silicate**); but the best sources of this metal are certain mineral springs (discovered in Cornwall and brought into notice in 1864), in which it exists as chloride. In the metallic state lithium is a chemical curiosity, and oxidizes so readily that it requires to be kept from the air. It may be prepared from its chloride by electrolysis. This metal is harder than **potassium,** but softer than **lead**; it is ductile, and is remarkable as being the lightest known solid. When heated in the air it burns, forming an oxide.

(*For detection and separation of Lithium, see Author's* **Analytical Chemistry**, *page* 46.)

AMMONIUM. Symbol, Am (NH_4). Atomic Weight, 18.

The existence of this metal in the free state is still a doubtful point. Some

chemists say that it has been isolated, and takes the form of a very volatile deep blue liquid, decomposing rapidly at the ordinary temperature of the air, and only capable of existing in the almost entire absence of heat, and under very great pressure. It is quite certain, however, that it may be obtained by the action of **sodium** and **mercury**, with which it forms an amalgam when these metals are placed in contact with a concentrated solution of **ammonium chloride** (NH_4Cl).

$$Na_2Hg + 2NH_4Cl = Hg(NH_4)_2 + 2NaCl.$$

This amalgam rapidly splits up :—

$$2Hg(NH_4) = Hg_2 + 2NH_3 + H_2.$$

Combinations of ammonium with a volatile acid are entirely volatile; with a fixed acid, such as **phosphoric** or **boracic**, the acid remains. This metal is monad in all its compounds.

(*For detection and separation of Ammonium, see Author's* **Analytical Chemistry**, *page* 48.)

SODIUM (*Natrium*). **Symbol, Na. Atomic Weight, 23. Specific Gravity, ·972. Melting Point, 207° F.**

Sodium salts are almost universally distributed in nature. The **chloride** ($NaCl$) constitutes a large proportion of the residue of sea-water. The **carbonate** (Na_2CO_3) was, in former times, almost entirely obtained from the ashes of marine plants. It is now, however, prepared from the chloride, either by Leblanc's process or by a new mode, called the *ammonia process*, which has been devised by R. Wagner (see Carbonates). The metal is prepared by heating a mixture of **sodium carbonate** and charcoal, in the manner adopted for the preparation of potassium, the next metal to be described. In its general properties sodium resembles potassium; but its combination with other bodies is attended with less violence, and the hydrogen it evolves when brought into contact with water, does not burst into flame unless the water be heated, or the sodium kept stationary.

(*For detection, separation, and estimation of Sodium, see Author's* **Analytical Chemistry**, *pages* 47 *and* 176.)

POTASSIUM (*Kalium*). **Symbol, K. Atomic Weight, 39·1. Specific Gravity, ·865. Melting Point, 144° F.**

Compounds of potassium are found in the ashes of most plants, in many waters, and in combination with silicic acid in several minerals. Potassium may be obtained by calcining **potassium bitartrate** (thus converting it into a mixture of **potassium carbonate** and **carbon**), and heating the residue to whiteness in a suitable retort, having adapted to it a condenser containing mineral naphtha. The metal is collected in small globules, which, on exposure to the air, are almost instantaneously oxidized, the oxide (K_2O) being formed.

In contact with water, at any temperature, potassium becomes sufficiently hot to inflame the hydrogen, which it displaces as the gas escapes. By this displacement **potassium hydrate** is formed :—

$$K_2 + 2H_2O = 2KHO + H_2.$$

The flame of the escaping hydrogen is tinged purple or violet by a trace of potassium vaporized by the heat. With all colourless acids, potassium forms colourless salts, and always behaves as a monad.

(*For detection, separation, and estimation of Potassium, see Author's* **Analytical Chemistry**, *pages* 47 *and* 175.)

SILVER (*Argentum*). **Symbol, Ag. Atomic Weight, 108. Specific Gravity, 10·47. Melting Point, white heat.**

The Hartz mountains in Germany, Kongsberg in Norway, and the Andes of America appear to be the seats of the chief silver mines. This beautiful metal is found in the forms of sulphide, chloride, iodide, and bromide; and occasionally it occurs almost pure. The ore, having been powdered and mixed with common salt, is subjected to a low red heat in a suitable furnace, the result being that any **sulphide** of silver present is transformed into **chloride.** The whole is then transferred to a cylindrical vessel revolving on its axis, into which are likewise introduced water and scraps of iron, the arrangement and its contents being kept in motion until the **silver chloride** is reduced by the iron to metal. Mercury is now poured on the mass, and the trituration repeated when the mercury unites with the silver, gold, and metallic copper, producing a fluid amalgam which is readily separated from the mud in the vessel by subsidence and washing. A strong linen cloth is presently brought into requisition, through which the amalgam is strained, the solid portion remaining being subjected to distillation, by which its mercury is volatilized and the impure silver left.

Every specimen, nearly, of native lead sulphide contains silver; but its extraction rarely pays for the expense.

Silver is also obtained by roasting the ore with pyrites, which converts the mass into **argentic sulphate,** the heat being so regulated that the **ferrous sulphate,** also produced, becomes decomposed towards the end of the process. Metallic copper is then introduced, which decomposes the argentic sulphate, when a deposition of metallic silver follows, leaving **cupric sulphate** in solution; thus yielding a product of great commercial value:—

$$Ag_2SO_4 + Cu = Ag_2 + CuSO_4.$$

Chemically pure silver may be prepared from any alloy containing it, such as a silver coin, by dissolving the article in dilute **nitric acid** aided by heat. The addition of **hydrochloric acid** will precipitate the silver in the form of **chloride,** leaving the other metals in solution. The **argentic chloride** having been collected and washed with boiling water, may now be reduced to the metallic state by any of the following processes:—

I. By fusing it with a mixture of potassium with **sodium carbonate**:—

$$2AgCl + KNaCO_3 = Ag_2 + KCl + NaCl + CO_2 + O.$$

(This is the B.P. process.)

II. By boiling with an alkaline solution of **glucose.** (**Argentic chloride,** by the action of potassium hydrate, yields **argentic oxide,** from which glucose reduces the metal.)

III. By reducing the freshly precipitated **chloride** with **zinc** and very dilute **sulphuric acid**:—

$$4AgCl + Zn_2 = 2ZnCl_2 + 2Ag_2.$$

Silver requires the power of a white heat in order to melt it; and although, when in a state of fusion in contact with the air, it absorbs oxygen, this gas does not combine with it to form an oxide, but is entirely rejected by the metal during the process of cooling. Silver is not acted upon either by cold **hydrochloric** or **sulphuric acids,** but on being boiled with the latter it dissolves, forming argentic sulphate:—

$$Ag_2 + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

The best solvent for silver is dilute **nitric acid,** in which it dissolves freely on the application of a gentle heat, and forms argentic nitrate.

$$3Ag_2 + 8HNO_3 = 6AgNO_3 + 2NO + 4H_2O.$$

When silver is digested in pure strong nitric acid (sp. gr. 1·42), it dissolves only by the application of heat, but the presence of even a trace of nitrous acid causes immediate action. It combines directly with **sulphur, chlorine, iodine,** and **bromine.** By the action of **sulphuretted hydrogen** it is blackened :—

$$Ag_2 + H_2S = Ag_2S + H_2$$

Silver is monad in all its compounds, **silver chloride** being AgCl, **sulphate** Ag_2SO_4.

(*For detection, separation, and estimation of Silver, see Author's* **Analytical Chemistry**, *pages 27 and 165.*)

Class II. DYADS.

Group 1. consists of the three metals, **calcium, strontium,** and **barium,** which unite with oxygen to form oxides called "alkaline earths." Like the former class, they each form but one chloride, but their carbonates are wholly insoluble in water.

Group 2. The resemblance between **cadmium, zinc,** and **magnesium** consists in the fact that they are volatile at high temperatures, burning when heated in the air; that they each form only one oxide and one chloride; and that they displace the hydrogen from dilute acids. Formerly, magnesium was regarded as one of the earth metals, but it is now held to evince a closer analogy to zinc.

Group 3. **Copper** and **mercury** are powerless to decompose water at any temperature, but are themselves oxidized by nitric and strong sulphuric acids, and they each form two chlorides and two oxides.

CALCIUM. Symbol, Ca. Atomic Weight, 40. Specific Gravity, 1·5778.

Of all the alkaline earthy metals, calcium is the most copiously distributed, entering into the composition of entire mountain ranges; and yet it never occurs in a free state, but always in combination with other substances. Its compounds exist in the forms of **carbonate, tungstate, sulphate, nitrate, silicate, arseniate, chloride,** and **fluoride,** in rocks and earths; as **carbonate** and **phosphate** in animal bones; as **carbonate** in the shells of crustaceæ and testaceæ; and it exhibits its presence in the ash of nearly every plant, and is **held in solution by all waters.**

The metal may be procured by the electrolysis of **calcium chloride,** or by the action of **sodium** vapour upon the same :—

$$2CaCl_2 + 2Na_2 = Ca_2 + 4NaCl.$$

As this metal rapidly oxidizes when in contact with air, especially if it be moist, preservation in mineral naphtha is necessary. In colour, ductility, malleability, and hardness, it resembles gold. Heated in the air on platinum foil over a spirit-lamp, it oxidizes with a brilliant flash. Of its compounds with other metals comparatively little is at present known. It forms an amalgam with mercury, but as yet, in the arts, calcium has received no practical application. Thrown on water or on acids it ignites.

The common forms of calcium carbonate are *limestone* and *marble,* while its rarer and purer states are *calc spar* and *arragonite.*

(*For detection, separation, and estimation of Calcium, see Author's* **Analytical Chemistry**, *pages 45 and 173.*)

STRONTIUM. Symbol, Sr. Atomic Weight, 87·5. Specific Gravity, 2·5418.

This metal takes its name from Strontian, in Argyleshire, where it was first observed in the form of carbonate in 1787; and it has since been detected, to

limited extent, in a salt spring at Eger, in sea-water, and in the mineral waters of Kaiser Franzensbrunnen. The native **carbonate** (*strontianite*, $SrCO_3$) and the **sulphate** (*celestin*, $SrSO_4$) are the chief sources of strontium, which in some respects resembles calcium and barium. This metal resembles calcium in possessing a similar yellow colour; but it oxidizes in the air with much greater rapidity, and it ignites when thrown upon water and on acids. Strontium possesses no pharmaceutical interest, its use being almost altogether limited to pyrotechnical display. The strontium nitrate is invaluable for this purpose owing to the brilliant crimson colour it may be made to communicate to flame.

(*For detection, separation, and estimation of Strontium, see Author's* **Analytical Chemistry**, *pages 44 and 174.*)

BARIUM. Symbol, Ba. Atomic Weight, 137. Specific Gravity, 4. Melting Point, below redness.

The metal barium, although as yet unapplied to any practical purpose in the arts or sciences, is peculiar on account of the great density of its compounds. It is from this circumstance that its name has been taken from the Greek word, βαρύς, heavy. Its chief sources are the native **carbonate** (*Witherite*, $BaCO_3$) and **sulphate** (*barytes*, or *heavy spar*, $BaSO_4$). From the former (barium carbonate) the rarer barium salts are prepared, whilst from the latter, a substitute for white-lead, used in oil painting, is derived.

Never found uncombined, it is obtained by passing **sodium vapour over fused barium chloride**, or by the electrolysis of the latter:—

$$2BaCl_2 + 2Na_2 = Ba_2 + 4NaCl.$$

Barium is ductile, and may be hammered out into a sheet; but as it oxidizes very rapidly in the air, these useful properties give it no practical utility. Heated in the air, it oxidizes with a dark red light, and with a greenish flame before the oxy-hydrogen blowpipe.

(*For detection, separation, and estimation of Barium, see Author's* **Analytical Chemistry**, *pages 43 and 173.*)

MAGNESIUM. Symbol, Mg. Atomic Weight, 24. Specific Gravity, 1·7430. Melting Point, 752° F.

Magnesium is usually extracted from *dolomite* (**magnesium** and **calcium carbonate**) or from its various **silicates**. It also occurs in springs in the form of *Epsom salts* (**magnesium sulphate**) in sea-water; in the structure of animals and plants; and in combination with acids derived from organic sources. *Magnesia alba* (**magnesium carbonate**) was formerly used in Rome as a medicine about the commencement of the 18th century; but it was Sir H. Davy who first obtained the pure metal, which may be eliminated by electrolysis, as follows. Introduce into the bowl of a common tobacco-pipe, a mixture of four parts **magnesium chloride**, three parts **potassium chloride**, with a little **ammonium chloride**. Heat the bowl over the flame of a spirit lamp or Bunsen's burner, the negative pole being an iron wire passed up the pipe stem, and the positive pole a fragment of coke, which must touch the surface of the fused contents, when the metal will appear in the form of globules. For commercial purposes, magnesium is produced by heating together to bright redness, in a covered earthen crucible, a mixture of six parts **magnesium chloride**, one part fused **sodium chloride**, one part pulverized **calcium fluoride**, and one part of **sodium**, when the metal collects in large globules.

In dry air magnesium oxidizes with difficulty, but a moist atmosphere quickly converts it into the oxide. Strongly heated, as when being held in the

flame of a lamp or gas jet, it ignites, burns with an intense white light, and deposits magnesium oxide. The metal is rapidly soluble in very dilute **hydrochloric** and **sulphuric acids**, with the evolution of **hydrogen**; but it is only slowly soluble in strong **sulphuric acid**. When thrown into strong **hydrochloric acid** it momentarily takes fire. In its behaviour it is invariably a dyad. It forms a solid amalgam with mercury, either when the two are heated together or when produced by electrolysis in the presence of the latter metal.

The chief native magnesium silicates may be noted to be as follows :—

Chrysolite . . .	Mg_2SiO_4.
Mica or Talc . . .	$4MgSiO_3SiO_24H_2O$.
Meerschaum . . .	$2MgSiO_3SiO_2$.

Soapstone is magnesium aluminium silicate, while *augite* and *hornblende* are magnesium and calcium silicates with a little iron.

(*For detection, separation, and estimation of Magnesium, see Author's* **Analytical Chemistry**, *pages* 45 *and* 174.)

ZINC. Symbol, Zn. Atomic Weight, 65. Specific Gravity, from 6·8 to 7·2. Melting Point, 773° F.

Zinc is largely found in the forms of **carbonate** (*calamine*), **sulphide** (*blende*, or *black jack*), and **oxide** (*red zinc-ore*); and it appears in less abundance as **aluminate, arseniate, phosphate**, and **sulphate**; but the most valuable of all the zinc ores is the *calamine*, or native **carbonate**, so named on account of the structural resemblance of the mineral to a reed. Although not usually a constituent of plants, this metal has been discovered in the ash of the *Viola calaminaria*, a violet which flourishes in Rhenish Prussia on the *débris* of the calamine mines in that district. Zinc is extracted as follows :—

The ore, after subjection to a preliminary calcination, is mixed with half its weight of powdered charcoal, anthracite, or coke, and heated in muffles furnished with a rectangular flue, when the mingled vapours of carbonic oxide and zinc pass off, and the latter, on condensing, drops from the opening in a liquid condition. As a secondary product in the smelting of lead ores, zinc is not disregarded. Provision is usually made for the condensation of the fumes, which are received upon a slanting stone (called at Goslar, in the Hartz mountains, the *zinc stool*), from whence the metal is collected, melted in iron pots, and poured out on tables.

The change effected on zinc ore in the furnace is as follows :—

$$1.\ ZnCO_3 = ZnO + CO_2, \text{ or } 2ZnS + 3O_2 = 2ZnO + 2SO_2.$$
$$2.\ 4ZnO + C_2 = 2Zn_2 + 2CO_2.$$

The first portions of the zinc which volatilize, are generally rendered impure by the presence of **cadmium** and **arsenic**. On this account they are occasionally rejected, or are subjected to special purification. When the metal is strongly heated it vaporizes, and the fumes burn in the air with a brilliant white flame, resulting in the formation of **zinc oxide**. Zinc is readily soluble in dilute **sulphuric, hydrochloric**, and **nitric acids**. It combines directly with **chlorine, bromine**, and **iodine**; in all its compounds behaving as a dyad. Cold strong **sulphuric acid** has little or no action upon zinc, but the dilute acid forms **zinc sulphate** with the evolution of hydrogen. Hydrogen is likewise evolved when the metal is treated with **hydrochloric acid**, the result being **zinc chloride**. Tolerably strong **nitric acid** unites with it, and forms **zinc nitrate**, with the evolution of nitric oxide; whilst very dilute **nitric acid** in forming **zinc nitrate** produces **ammonia**. This metal is soluble in **potassium** and **sodium hydrates**, with the evolution of hydrogen.

Zinc is brittle, and slowly tarnishes or oxidizes when exposed to the air; if heated from 248° to 292° Fahrenheit, it becomes malleable, and and may be hammered or rolled without risk of disintegration, retaining this valuable property on cooling. This is how the sheet-zinc of commerce, which is now put to so many varied and important uses, is made. The so called "**galvanized iron**" is simply sheet iron upon which a coating of zinc has been deposited of sufficient thickness to prevent rusting for a long time. **German silver** is a compound consisting of nickel and zinc.

(*For detection, separation, and estimation of Zinc, see Author's* **Analytical Chemistry**, *pages* 4[illegible] *and* 171.)

CADMIUM. Symbol, Cd. Atomic Weight, 112. Specific Gravity, 8·60. Melting point, 500° F.

Bishopstown in Renfrewshire has the distinction of producing the only pure native source of this metal at present known. It occurs there in the form of **Sulphide**, and passes under the name of *Greenockite*. In small quantities it is found also in the *blende* of Hungary and Nussère, and in the zinc ores from Freiberg, Mendip, Silesia, in the smelting of which it is obtained as a secondary product of importance. Owing to its greater volatility, its vapour appears among the first results of distillation. The distillate is dissolved in warm **hydrochloric acid**, and the metal afterwards precipitated by the addition of **sulphuretted hydrogen**, which throws it down as a yellow sulphide, and yields a pigment highly esteemed for its rich golden colour and permanence. This sulphide, dissolved in hydrochloric acid and treated with metallic zinc, deposits the metal.

$$2CdCl_2 + Zn_2 = Cd_2 + 2ZnCl_2.$$

It volatilizes at about 650° F. without odour, and is white with a blue tinge, flexible, malleable, lustrous, and ductile. Always dyad, it combines directly with **chlorine**, **iodine**, and **bromine**, and is dissolved with ease by **hydrochloric** and **nitric acids**, but with difficulty by **sulphuric**. Heated in contact with the air, it ignites, producing brown cadmium oxide. It forms a silvery alloy with platinum, and yellowish with copper.

(*For detection, separation, and estimation of Cadmium, see Author's* **Analytical Chemistry**, *pages* 52 *and* 167.)

COPPER (*Cuprum*). **Symbol, Cu. Atomic Weight, 63·4. Specific Gravity, 8·96. Melting point, bright red heat.**

From the fact that copper is found naturally in the metallic state, and is ductile and malleable immediately after fusion, we have no difficulty in arriving at the reason why this metal should have been used by primitive man for the fashioning of agricultural implements, rude tools, and weapons of war, long before iron. Copper is abundantly distributed, and the following ores are those which exhibit its usual form:—*copper pyrites* (**cuprous sulphide with ferric sulphide**, $Cu_2SFe_2S_3$), *malachite* (**cupric carbonate** with **cupric hydrate**, $CuCO_3,Cu2HO$), **cupric sulphide** (CuS), and **cupric sulphate** ($CuSO_4$). The metal is usually obtained either from the copper pyrites or from the cupric sulphide. These are roasted in the air till part of the **sulphide** is converted into **oxide**; and when the mass is heated, without contact with the air, metallic copper and **sulphurous anhydride** result.

1. $2CuS + 2O_2 = 2CuO + SO_2.$
2. $4CuO + 2CuS = 3Cu_2 + 2SO_2.$

In order to remove a little **cuprous oxide** which generally remains undecom-

posed, the fused metal is stirred with a piece of green wood. Copper, although a dyad metal, possesses the property of becoming self-saturated, Cu'', producing $(Cu_2)''$. The former is the radical of *cupric* salts, the latter of *cuprous*. The cupric salts are by far the more important, none of the cuprous being either known in commerce or used in medicine.

This metal resists the action of either **dilute sulphuric** or **hydrochloric acids**; but **strong sulphuric acid**, aided by heat, converts it into **cupric sulphate**, with the evolution of **sulphurous anhydride**. It is acted upon by **nitric acid** whether strong or dilute, which attacks it readily, forming **cupric nitrate**, with the evolution of **nitric oxide**. When the acid is hot and strong, a little nitrogen is also formed; and when cold and dilute, the evolved gas contains a little nitrous oxide. When heated in the air, copper oxidizes without inflaming.

Our bronze coinage is an alloy into which 4 per cent. of tin and 1 per cent. of zinc with 95 per cent. of copper enter. Copper unites with a great number of other metals, such as gold, silver, cadmium, iron, lead, aluminium, antimony, and even with arsenic, forming with the last named, very definite, grey, brittle compounds.

(*For detection, separation, and estimation of Copper, see Author's* **Analytical Chemistry**, *pages* 31 *and* 167.)

MERCURY (*Hydrargyrum*). **Symbol, Hg. Atomic Weight, 200. Specific Gravity, 13·59. Boiling Point, 662° F.**

Apart from the singularity of its appearance, mercury is deserving of special attention on account of the varied and important purposes to which it is applied both in pharmacy and in the arts. Known from the earliest times, *cinnabar* (**mercuric sulphide**) was employed as a pigment by the ancients; *calomel* (**mercurous chloride**) was familiar to the alchemists; and *corrosive sublimate* (**mercuric choride**) at an early period was common among the Arabians.

Although often found in the form of globules distributed throughout the substance of its ores; in combination with gold and silver, as amalgams; as **chloride, iodide,** and rarely as **selenide,**—it is in the form of **sulphide** that we meet the source from which the bulk of the mercury of commerce is obtained. The chief *cinnabar* mines are those of Almaden in Spain, and Idria in Illyria; but in Bavaria, Bohemia, Hungary, and some other parts of Europe the ore occurs sparingly; whilst in China and Japan, Peru and California, it is much more extensively found.

Cinnabar is deprived of its mercury by two methods, *i.e.*, by roasting in the air, or by being heated with quicklime (**calcium oxide**). By the first process the following effect is produced :—

$$2HgS + 2O_2 = Hg_2 + 2SO_2$$

When **calcium oxide** is used, **calcium sulphide** is formed, oxygen being evolved :—

$$2HgS + 2CaO = Hg_2 + 2CaS + O_2.$$

By the action of metallic iron we can also obtain mercury from cinnabar :—

$$2HgS + Fe_2 = Hg_2 + 2FeS.$$

The boiling point of mercury being 662° F., in all the preceding processes it distils over, and condenses in chambers having an inclined floor, which enables the metal to run out and be collected. Its purification is accomplished by pressure through wash-leather and redistillation.

In atomicity mercury is a dyad, although it has the property of self-

saturation so as to produce $(Hg_2)''$, the radical of *mercurous* salts, Hg″ being the radical of *mercuric* compounds.

Mercury is rapidly oxidized on exposure to the air, when at a temperature approaching 662° F., but is only slowly oxidized by moist air at the normal heat of the surrounding atmosphere.

Hydrochloric and **dilute sulphuric acids** exert no action upon this metal; but **strong, boiling sulphuric acid** converts it into **sulphate,** with the evolution of **sulphurous anhydride.** Dilute **nitric acid** dissolves it, and a mixture of **mercuric** and **mercurous nitrates** results, unless the temperature of the acid has been low throughout the progress of the operation, in which case only the latter is obtained. The action of *pure* nitric acid of 1·42 specific gravity requires heat unless some nitrous acid be present.

Mercury forms amalgams with many metals, notably zinc, lead, gold, silver, potassium and sodium. The latter compound is extensively used in organic research. Tin amalgam is used for "silvering" mirrors.

(For detection, separation, and estimation of Mercury, see Author's **Analytical Chemistry,** *pages 28, 39, and 166.)*

Class III. TRIADS.

The only metal of interest to us in this group is :—

GOLD (*Aurum*). **Symbol, Au. Atomic Weight, 196·7. Specific Gravity, 19·50. Melting point** (*average*), **2435°** F. (*Pouillet*, 2192°; *Marveau*, 2518°, *Daniell*, 2596°).

If the eagerness with which any natural production is sought after by all conditions of civilized man be a correct index of its value, then indeed gold stands pre-eminent. But this beautiful and much desired metal has special merits of its own, which would amply recommend it, even were it as cheap as iron.

Probably no substance amidst all our geological treasures is more impartially distributed over the globe than gold, inasmuch as, in some form or other, it is found in every country under the sun. In Europe our chief sources of supply are Transylvania and Hungary; but it occurs in notable quantities in the sands of the Rhine, the Aar, and the Reuss; it lurks amidst the recesses of the Alps, Monte Rosa, and Val d'Aosta; and to come nearer home, we are occasionally gratified by a glimpse of its glittering particles in the streams of Cornwall and amidst the rocky fastnesses of Scotland and Ireland. The Ural mountains, Siberia, the Altai and Cailas mountains, China, Ceylon, and the Eastern Archipelago, all yield a copious Asiatic tribute of gold; Africa has its mines at Kordofan, between Darfour and Abyssinia, the Ophir of Solomon is supposed to have been on the coast opposite the island of Madagascar; and we have learnt from Dr. Livingstone and other travellers, of rivers that teem with golden sand. In the New World we find gold abundant in Brazil, New Granada, and Chili; in Mexico, California, British Columbia, and Nova Scotia. And lastly, Australia and New Zealand produce the much coveted metal in abundance.

Gold is invariably found in the metallic state; in the sands of rivers in the form of dust, in auriferous quartz as grains; and under the surface of the earth in the alluvial deposits formed by the disintegration of auriferous strata.

Probably the purest samples yet obtained are those from Schabrowski in the Ural mountains, one of which was found to contain 98·96 per cent. of the pure metal. But our Australian gold does not compare unfavourably even with this remarkable assay, as it averages from 96 to 96·6 per cent.

The extraction of this metal from the mineral substances mechanically associated with it is remarkably simple. It consists in washing with water to remove earth and clay, leaving the metal, either pure or alloyed, behind; or by treating the bruised auriferous rock with mercury, thus forming an amalgam, which is afterwards purified and separated into its constituent parts by pressure through wash-leather, the removal of the mercury by distillation, and treatment with nitric acid to dissolve out the silver.

Gold does not combine directly with sulphur, although it is tarnished by the presence of sulphuretted hydrogen.

It is insoluble in all simple acids, but dissolves in **nitro-hydrochloric acid,** and in solutions of **chlorine, iodine,** and **bromine.** In its compounds it acts as a triad, but may by partial self-saturation act as a monad. The chloride produced by its solution in the first-mentioned solvent is **auric chloride** ($Au'''Cl_3$).

Its oxide does not combine with oxy-acids to form salts. In the air, gold undergoes no change, not even when strongly heated; but under the effect of a powerful current of electricity, thin leaves or minute wires are volatilized. Gold forms compounds with most metals; the copper alloy is that used for coin, jewellery, etc. **Gold solder** is frequently partly silver as well as copper.

(*For detection, separation, and estimation of Gold, see Author's* **Analytical Chemistry,** *pages* 35 *and* 168.)

CLASS IV. TETRADS.

ALUMINIUM. Symbol, Al. Atomic Weight, 27·4. Specific Gravity, 2·56 to 2·67.

Aluminium occurs in nature as oxide (Al_2O_3), and in many minerals as silicate. It is prepared by heating its chloride or fluoride with metallic sodium.

$$Al_2Cl_6 + 3Na_2 = Al_2 + 6NaCl.$$

This metal does not readily oxidize; is but slowly attacked even by boiling nitric acid. **Hydrochloric acid** dissolves it readily, with the evolution of **hydrogen.**

$$Al_2 + 6HCl = Al_2Cl_6 + 3H_2.$$

It is not acted upon by **dilute sulphuric acid,** and scarcely at all by pure **acetic acid.**

In solutions of **alkaline hydrates** it dissolves readily, producing **aluminates** and evolving **hydrogen**:—

$$Al_2 + 2KHO + 2H_2O = K_2Al_2O_4 + 3H_2.$$

In no compound does the single atom, Al, exist, but always the double atom, Al_2, which acts as a hexad.

Great hopes were raised with respect to the application of aluminium in the arts, owing to its extreme lightness and the manner in which it resists oxidation. Deville was the first chemist who succeeded in obtaining it in a pure metallic state. The so-called "aluminium gold," is nine-tenths copper and one-tenth aluminium, and is also known as aluminium bronze.

(*For detection, separation, and estimation of Aluminium, see Author's* **Analytical Chemistry,** *pages* 39 *and* 172.)

MANGANESE. Symbol, Mn. Atomic Weight, 55. Specific Gravity, 8.

Manganese occurs in the ashes of plants and in several ores, of which *pyrolusite* (**manganic dioxide,** MnO_2) is the chief. It is prepared by igniting this mineral, mixing the product with charcoal, and subjecting the combina-

tion to intense heat. The metal so obtained is not readily fusible, and is quickly oxidized by exposure to the air. It is a tetrad in atomicity, but two of its powers are generally latent, and thus it behaves as a dyad. The manganic salts are but little known, the manganous only being worthy of attention. Manganese is practically insoluble in cold **strong sulphuric acid**, but on heating it dissolves, evolving **sulphurous anhydride**. It is freely soluble in very **dilute sulphuric** and **hydrochloric acids**, with the evolution of **hydrogen**; and it is also readily attacked by **nitric** and **acetic** acids. Manganous salts are the only ones produced by the direct solution of the metal in acids. The material known as "*spiegel eisen*" (mirror iron) and employed in commerce as an addition to improve the quality of iron and steel, is an alloy of about four parts of iron to one of manganese.

(*For detection, separation, and estimation of Manganese, see Author's* **Analytical Chemistry**, *pages 40 and 171.*)

IRON (*Ferrum*). Symbol, Fe. Atomic Weight, 56. Specific Gravity, 7·79.

If we consider the astonishing strides made in human industry, and to what an extent civilization has spread since the universal use of iron among cultivated nations, we cannot fail to admit that although this metal may not be intrinsically the most valuable, it is by far the most important. In the metallic state it is of very limited occurrence, and with the exception of a trifling vein in the state of Connecticut, and isolated masses found on the surface in various parts of the world, supposed to be of meteoric origin, it has rarely been seen as such. The metal is contained in many ores, the most notable being the **ferrous carbonate** ($FeCO_3$) or *spathic ore*, the **magnetic oxide** (Fe_3O_4), the **ferric oxide** (Fe_2O_3); or *hæmatite*, and the **ferrous disulphide** (FeS_2) or *iron pyrites*. The forms of the **ferrous carbonate**, "blackband" and "clayband" ironstones, are the ores from which iron is usually extracted in this country. These are first subjected to a preliminary roasting in a kiln or in heaps, to drive off water and carbonic acid gas, and then introduced into a blast furnace along with coke and limestone, where the ores are reduced at first to the metallic condition and afterwards the carbon present unites by *cementation* with the metal to form a "carbide", the silica and alumina contained in the ore uniting with the lime to form fusible slag. The blast of air used is heated to a temperature capable of melting lead, before it is allowed to enter the furnace; and the operation proceeds night and day, fresh ingredients being poured in at the top of the furnace while the melted iron is run off at the bottom at convenient intervals into furrows prepared in a bed of sand, where it solidifies and is then known as *pig iron*. In this form the metal contains proportions of carbon, phosphorus, and silicon, and is necessarily brittle and without a trace of malleability, but by heating it in a reverberatory furnace in a blast of air, accompanied by continual movement (technically termed "puddling"), and subjecting the mass to the strokes of a steam hammer, the impurities are to a great extent removed and although the iron becomes less fusible, it acquires that tenacity which confers malleability, and is known as *wrought* or *bar* iron.

By heating bars of iron for several hours in charcoal, the metal combines with about one and a half per cent. of carbon, and is converted into *steel*. The process is termed *cementation*, and the product, "blister steel." This useful variety of iron may also be prepared directly from the *pig* by the Bessemer process, which consists in melting the metal, and forcing a blast of air through the fluid mass until all impurities are burnt out. At this stage just sufficient crude cast iron is added to yield the necessary carbon to convert the whole into steel, when the contents of the crucible are run into moulds.

Steel is rendered hard for the manufacture of edged tools by heating it to about 470° F., and suddenly cooling; or elastic, by heating to 550° F., and quickly cooling as before. This process is called the "tempering of steel." Iron alloys itself readily with other metals when they are heated with it.

Iron is truly a tetrad, but it never acts as such. In the ferrous compounds it behaves as a dyad, and in the ferric as a hexad. These facts are explained by the following formulæ:—

Iron in the free state. $Fe \equiv Fe = Fe_2.$

Ferrous chloride. $=Fe<^{Cl}_{Cl} = Fe''Cl_2.$

Ferric chloride. $^{Cl}_{Cl}{>}\!\!-\!Fe-Fe\!-\!{<}^{Cl}_{Cl}$ with Cl — Cl on each side: $Cl_3 \equiv Fe-Fe \equiv Cl_3 = Fe^{vi}_2Cl_6.$

Strong cold **sulphuric acid** has little or no action upon iron, but the dilute acid dissolves it, forming **ferrous sulphate** and liberating **hydrogen.** It is also soluble in **hydrochloric acid,** forming **ferrous chloride** and likewise evolving **hydrogen.** With tolerably strong **nitric acid,** or with a dilute acid by the aid of heat, **ferric nitrate** is produced, and **nitric oxide** evolved; but with *very dilute* and *cold* nitric acid, ferrous nitrate is formed, with the production of nitrous oxide, or ammonium nitrate is yielded in solution, without the evolution of any gas:—

$$2Fe_2 + 10HNO_3 = 4Fe2NO_3 + NH_4NO_3 + 3H_2O.$$

True theoretical nitric acid, entirely free from water, does not attack iron in the least; and if the metal after such treatment be plunged into B.P. acid (1·42 sp. gr.) it will not even then be affected, but the moment it is touched with a piece of copper the action will set in with great rapidity. This curious behaviour is called **passivity.** (*See* **Nitric Acid,** Chap. X.)

(*For detection, separation, and estimation of Iron, see Author's* **Analytical Chemistry,** *pages* 37, 158, *and* 171.)

COBALT. Symbol, Co. Atomic Weight, 58·8. Specific Gravity, 8·54.

Cobalt is one of the scarce metals, and has never been found in the metallic state, except as a component part of meteorites, in which it occurs sometimes to the extent of one per cent., associated with nickel and iron. The pure metal has a steel grey colour, with an inclination towards red; but in the polished form is white. Less easily melted than gold, it is subdued by the heat of the furnace sooner than iron, and, like the latter, is magnetic: a property which the strongest red heat cannot eradicate, although it is destroyed by the presence of a minute quantity of arsenic.

Solution of cobaltous chloride is used at Sèvres to counteract the yellow colour of the finer kinds of porcelain, a bright clear tint of any desired intensity being thus produced according to the proportion of the cobalt solution that may have been employed.

Cobalt is found in similar ores to the metal nickel, and is extracted therefrom in a precisely similar manner. (*See* **Nickel.**)

It is usually a dyad, and, when so, forms cobaltous salts. These salts, when anhydrous, are blue; when hydrated, pink. Its behaviour with acids is similar to nickel.

(*For detection, separation, and estimation of Cobalt, see Author's* **Analytical Chemistry,** *pages* [illegible])

NICKEL. Symbol, Ni. Atomic Weight, 58·8. Specific Gravity, 8·80.

This beautiful metal has much in common with cobalt and iron, and is constantly found in association with them, both in various ores and in meteorites. Several of its properties fitting it for an alloy, it is used in the proportion of 40 parts of nickel, 60 of zinc, and 100 parts of copper, for the production of the highly popular metal called *German silver*, or Nickel silver. This alloy is exceedingly malleable, and takes a high polish. Among all the metals, nickel is the only one possessing a name of opprobrium, which arose from the circumstance that in early days the ignorant German miners, having in vain tried to extort copper from its ore (the mono-arsenide, NiAs) in disgust bestowed the epithet upon it of *Kupfer-nickel*, or false copper.

This metal is found naturally in combination with arsenic and sulphur, and in order to get rid of these impurities the ore is roasted in a state of powder, at a moderate heat, by which preliminary operation the greater portion of its arsenic is volatilized, and the oxide of the metal remains. This is exposed to a white heat in a charcoal-lined crucible, the oxide having been previously carefully mingled with powdered charcoal. In order to obtain the resulting metal in ingots, the shapeless masses are fused at the strongest heat of a forge fire. This metal is also magnetic, but, unlike cobalt, it loses this property when heated to 662° F. It is usually a dyad; and the salts it forms when in this state, which are termed *nickelous*, are well-defined, and of a green colour. It dissolves when heated with hydrochloric or dilute sulphuric acid, with the evolution of hydrogen; and it is rapidly attacked by nitric acid.

(*For detection, separation, and estimation of Nickel, see Author's* **Analytical Chemistry**, *pages* 42 *and* 171.)

CERIUM. Symbol, Ce. Atomic Weight, 92. Specific Gravity, 5·5 @ 54° F.

Cerium is found in the form of *cerite*, a silicate obtained from Sweden. The metal is never seen in an isolated condition except as a chemical curiosity, when it usually appears as a grey powder, soluble in dilute acids, and decomposing water at a boiling heat with the evolution of hydrogen. Its only compound of interest to the pharmacist is **cerous oxalate** ($Ce''C_2O_4 3H_2O$).

(*For detection and separation of Cerium, see Author's* **Analytical Chemistry**, *page* 38.)

TIN (*Stannum*). **Symbol, Sn. Atomic Weight, 118. Specific Gravity, 7·29. Melting Point, 230° F.**

Tin is derived from an ore popularly called *tinstone* (SnO_2) by heating it with charcoal.

$$2SnO_2 + 2C_2 = Sn_2 + 4CO.$$

If the product be again heated, the pure metal fuses first, a less fusible alloy remaining solid, from which the fluid metal may be decanted. The chief sources of supply are Devonshire and Cornwall, although the mines of Malacca and Banca rank high in importance; and of late years the supplies from Australia have not only been considerable, but the tin from Melbourne occasionally contains so much gold that its extraction is profitable.

This metal does not oxidize at the ordinary temperature of the air, but when strongly heated it ignites, and stannic acid is formed. As regards atomicity, tin is usually tetrad, but by self-saturation is capable of behaving as a dyad. The compounds in which it exists in the former state are *stannic*, those in which it exhibits the latter, *stannous*. With lead, tin forms the alloy called *pewter*; with lead and bismuth, *Rose's metal*, an alloy which melts below

212° F. It is a component of bronze, bell metal, speculum metal, gun metal, Britannia metal, and "coarse" and "fine" solder. Tin is deposited on pins in the wet way and on "tin plate" by dipping the sheet iron in the melted metal, for the purpose of lessening the corrosive power of liquids and the atmosphere on the brass and iron respectively. Tin is difficultly soluble in **dilute sulphuric acid,** but when heated with the **strong acid** it forms **stannic sulphate,** and evolves **sulphurous anhydride. Nitric acid** converts the metal into white insoluble **metastannic acid. Dilute hydrochloric acid** is devoid of action, but by **boiling** with the strong acid **stannous chloride** is formed, and **hydrogen** evolved. **Nitro-hydrochloric acid** produces a mixture of **stannic** and **stannous chlorides.** Tin does not readily form salts with oxy acids.

(*For detection, separation, and estimation of Tin, see Author's* **Analytical Chemistry,** *pages* 35 *and* 169.)

PLATINUM. Symbol, Pt. Atomic Weight, 197·4. Specific Gravity, 21·50. Melting Point, *Oxy-hydrogen blowpipe.*

Platinum enjoys the remarkable distinction of being at once the heaviest substance at present known, the most refractory under the glow of the fiercest furnace; the most defiant to the solvent power of all individual acids; and the potent auxiliary of the laboratory, without the aid of which many of our most delicate and important investigations would be but imperfectly conducted. Like gold, it occurs in a metallic state in grains and little masses amidst the sand and *debris* of the Ural mountains, in various parts of Russia, in Brazil, Ceylon, and in the auriferous sands of some American rivers, but it has not as yet been detected in any rock, not even in the serpentine formation, although frequently discovered surrounded by such detritus as would lead to the inference that its matrix belonged to one of the earliest volcanic formations. The metal is purified by solution in nitro-hydrochloric acid; is precipitated by ammonium chloride, and calcination completes this preliminary process. It now appears in the form of an incompact mass, called **spongy platinum,** which requires the intense heat of the oxy-hydrogen blowpipe to accomplish its liquefaction. This is managed as follows:—A little furnace is constructed out of two solid pieces of lime, the lower fragment having a cavity hollowed out to contain the melted metal, with a notch at one side through which the crude platinum is gradually introduced in small pieces, and from which the fluid may in due time be poured. A cover of lime with a conical perforation on the top for the admission of the blowpipe is then fitted close, and the arrangement firmly braced together with iron wire. The tap admitting the hydrogen is then turned and the gas lighted at the notch in the crucible, the oxygen being slowly and gradually supplied. When the furnace is hot enough the platinum is introduced, piece by piece, through the side orifice. With the exception of iridium and rhodium, all metallic and other substances originally in the platinum are expelled; any sulphur, phosphorus, arsenic, and osmium there may be, are oxidized and driven off in vapour; palladium and gold are volatilized; and the iron and copper oxidize and disappear into the mass of the crucible. By this method about fifty pounds of platinum may be fused at one time. Previously to the application of the oxy hydrogen blowpipe to this refractory metal, it was obtained in a solid and compact form from the spongy condition by pressure, heat, and hammering. The loose and incoherent metal was rubbed down in a wooden mortar, and worked up into a paste with water, before being subjected to pressure in a brass conical mould. It was then dried, heated to whiteness in a furnace, and hammered, after which it acquired sufficient malleability and ductility to be rolled into plates or drawn out into wire.

Platinum in the finely divided state has the property of absorbing gases without combining with them. Of oxygen it is capable of condensing about four hundred volumes. The variety of platinum thus employed is known as **Platinum black,** and is prepared by boiling platinic chloride with glucose and sodium carbonate, when it deposits, leaving a colourless solution. As already mentioned, the most powerful furnace heat fails to cause even incipient fusion; and when subjected to the oxyhydrogen flame it does not oxidize. It remains perfectly insoluble in all simple acids; but **nitro-hydrochloric acid** colliquates it, **platinic chloride** ($PtCl_4$) being formed. When **potassium hydrate** is fused in platinum vessels, these are acted upon, and a **potassium platinate** results. For this reason, if alkalies are required to be fused, silver crucibles must be used. With several metals,—zinc and lead for example,—it forms alloys which are fusible by the heat of an ordinary furnace, as is likewise its compound with phosphorus.

Although platinum is a tetrad, it occasionally acts as a dyad.

(*For detection, separation, and estimation of Platinum, see Author's* **Analytical Chemistry,** *pages* 30 *and* 108.)

LEAD (*Plumbum*). **Symbol, Pb. Atomic Weight, 207. Specific Gravity, 11·45. Melting Point, 590° F.**

It is, perhaps, a fortunate circumstance that lead is a metal as abundant as it is useful, and that it is peculiar to no one part of the world. Yet, although fully twenty ores containing this metal are on the catalogue of the mineralogist, practically our sources of supply are confined to a few, the chief of which are *galena* (**plumbic sulphide,** PbS), *white lead,* or *cerusite* (**plumbic carbonate,** $PbCO_3$), and *anglesite* (**plumbic sulphate,** $PbSO_4$). Lead is usually extracted from the first mentioned, which is roasted in the air, being thereby converted into a mixture of plumbic sulphate and plumbic oxide, sulphurous anhydride being evolved:—

$$3PbS + 5O_2 = 2PbO + PbSO_4 + 2SO_2.$$

The whole is then strongly heated away from contact with the air, when the undecomposed *galena* acts upon both the oxide and the sulphate, the sole products being metallic lead and sulphurous anhydride:—

$$2PbO + PbSO_4 + 2PbS = 5Pb + 3SO_2.$$

Another process for the extraction of lead from its ore, is to roast *galena* until it is entirely converted into oxide, and then to reduce the result with charcoal:—

$$2PbO + C_2 = Pb_2 + 2CO.$$

Lead is rendered more fusible by adding arsenic, as is done in making shot, harder by being alloyed with antimony, as in type metal, and more fusible by tin. In its pharmaceutical salts lead is always dyad, its chloride being $PbCl_2$, its sulphate $PbSO_4$. When melted in contact with the air, this metal becomes covered with a crust of **plumbic oxide** (PbO). Lead is slowly oxidized by water when it contains fixed air. **Boiling sulphuric acid** converts it into **sulphate,** but it resists all action of **cold hydrochloric** and **sulphuric acids. Aqua regia,** however, converts it into **chloride.** Warm and dilute **nitric acid** dissolves the metal with ease, forming **plumbic nitrate** ($Pb''2NO_3'$), and evolving nitric oxide:—

$$Pb_3 + 8HNO_3 = 3Pb2NO_3 + 2NO + 4H_2O.$$

The oxide is acted upon by acetic, nitric, and nearly all acids, forming plumbic salts.

(*For detection, separation, and estimation of Lead, see Author's* **Analytical Chemistry,** *pages* 28 *and* 165.)

CLASS V. PENTADS.

BISMUTH. Symbol, Bi. Atomic Weight, 210. Specific Gravity, 9·90. Melting Point, 500° F.

Bismuth does not take rank among those metals which are universally distributed throughout the geological formation of every country, yet it possesses three most remarkable properties which are well worthy of attention. Of all metals it is the most diamagnetic; unlike other metals, when exposed to immense pressure, its density decreases (under 200,000 pounds the specific gravity falls from 9·90 to 9·546); and after being melted it expands on resuming the solid condition. This metal reaches us chiefly from Saxony, where it occurs in veins permeating clay-slate and gneiss, from Siberia, from Cornwall, and Cumberland. As a **sulphide** (Bi_2S_3) it is more abundant than in the native metallic state. Its preparation is as follows:—

The ore having been roasted, this reaction occurs:—

$$2Bi_2S_3 + 9O_2 = 2Bi_2O_3 + 6SO_2.$$

This **bismuthous oxide** is now heated with charcoal, when metallic bismuth and carbonic oxide result.

$$2Bi_2O_3 + 3C_2 = 2Bi_2 + 6CO.$$

Bismuth is a greyish metal with a pink tinge, which melts at 500° F. and volatilizes at a white heat. In dry air, at the ordinary temperature, it does not oxidize; but when strongly heated it burns with a blue flame. It easily dissolves in **nitric acid**, with the evolution of **nitric oxide.** Heated with **strong sulphuric acid, bismuthous sulphate** is formed, with the evolution of **sulphurous anhydride**; but it is altogether insoluble in **dilute sulphuric acid,** and nearly so in **hydrochloric,** even when heated. Its most remarkable alloy consists of one part of lead, one of tin, and two of bismuth, which melts at a little under the boiling point of water. The solder used in mending pewter requiring to be very fusible (otherwise the pewter itself would melt) has Bismuth added to lower the melting point. Type-metal sometimes contains this metal, which is utilized as a material whose great expansion on cooling admits of the production of very fine casts. It is a triad *in all compounds connected with Pharmacy.*

(*For detection, separation, and estimation of Bismuth, see Author's* **Analytical Chemistry,** *pages* 31 *and* 168.)

ANTIMONY (*Stibium*). **Symbol, Sb. Atomic Weight, 122. Specific Gravity, 6·70 to 6·86. Melting Point, 842° F.**

Antimony occurs naturally as sulphide, and is also found in combination with various metals. As *antimony ochre*, it usually takes the formula of Sb_2O_4; as *grey antimony*, Sb_2S_3; and as *antimony blende*, or *red antimony*, it presents a mixture of the first and second. The abundance of the grey (or black) ore abolishes any necessity for having recourse to any others, consequently their employment for the extraction of this metal is rare. Ores which are comparatively free from other metallic contamination are thus treated:—A portion is roasted until oxidized; mixed with the remainder, and again strongly heated. The Sb_2S_3 may be reduced in a different manner, by contact with **metallic iron,** or with an alkali and charcoal. Native **antimonious sulphide,** Sb_2S_3, occurs in mechanical combination with quartz and limestone. It may be separated from these by fusion, the heavy metallic portion sinking by the

law of gravity, and abandoning the impurities, which remain on the surface of the molten mass.

Arsenic being a contamination from which commercial antimony is rarely free, the use of the metal under consideration in medicine would doubtless be attended with the gravest results, were not some ready process available for its complete purification. The following method for the attainment of this object may be recommended. Two parts of dry sodium carbonate, mixed with five parts of sodium nitrate (or potassium nitrate, the former being preferable) and four parts of metallic antimony, are thrown into a red-hot crucible. The evolution of gas having ceased, the heat is increased until pressure with a spatula on the glowing mass proves that no cavities remain. Removed from the crucible whilst still soft, and having been reduced to powder on cooling, the result is rubbed in contact with boiling water, the surplus liquid being poured off from time to time. A smooth creamy mass having at length been produced, its freedom from alkaline matter is accomplished by further washing, decantation, and purification on a filter. Thus obtained, the powder, fused at a red heat with potassium hydro-tartrate (cream of tartar), on subsequent lixiviation with water, yields the metal.

Antimony is a brittle, silvery, and very brilliant substance, appearing in plates, or in rhombohedral crystals. The metal may be obtained in an amorphous state by electrolytic action. When fused it burns, forming antimonious oxide; but it does not oxidize at the ordinary temperature of the atmosphere. The oxide produced by combustion is nearly pure white. Should the metal at the commencement of its combustion emit a garlic-like odour, the presence of arsenic is indicated. Nitric acid oxidizes it, but fails to dissolve the product of its action, which, should the acid be very strong, becomes antimonic oxide, containing more or less antimonious oxide according as the acid used deviates from purity. Dilute sulphuric acid exerts no influence on this metal, although heating with a concentrated acid determines the production of a sulphate, with the evolution of sulphurous anhydride. Except when reduced to fine powder, boiling hydrochloric acid does not alter antimony.

There are two classes of antimony salts, in one of which the metal behaves as a triad, and in the other as a pentad. The former are named *antimonious salts*, and are the only ones possessing pharmaceutical interest; whilst the latter are termed *antimonic salts*. The maximum atomicity is the one by which we classify it, the lower being accounted for by the theory of self-saturation.

Many metals form alloys with antimony, the following being the most useful and interesting—

"Britannia metal," used for so many domestic articles. Type-metal, in which it is united with lead.

Copper antimoniae has the approximate composition Cu_2Sb_2, probably a mixture of $Cu_3''Sb_2'''$ and $Cu_3''Sb_2'''$, in nearly equal proportions. Its colour is violet, which does not in the least resemble that of a mere mixture of the two elements, and it is likewise very brittle.

Lead antimonide is harder than lead alone. When antimony is present to the extent of about twenty per cent., the alloy is recognised as type metal. The combination is denser (*i.e.*, it possesses a greater specific gravity) than the calculation from the respective quantities of the two metals indicates.

Silver antimonide is found native, and is precipitated from argentic nitrate by antimoniuretted hydrogen, evolved by the action of zinc and dilute sulphuric acid upon a solution containing an antimony salt. The full description of the formation of this body will be found under the heading **Arsenic**, among the Metalloids; the striking resemblance between the

reactions of antimony and those of that element being rendered evident by the adoption of such a course.

(*For detection, separation, and estimation of Antimony, see Author's* **Analytical Chemistry**, *pages* 34 *and* 169.)

Class VI. HEXADS.

CHROMIUM. Symbol, Cr. Atomic Weight, 52·2. Specific Gravity, 7·3.

The Shetland Islands contribute the ore, from which the metal may be extracted in considerable quantity. It is *chrome iron ore* ($FeCr_2O_4$). The metal, which, however, is of no commercial importance as yet, is obtained by igniting **chromic oxide** with charcoal at a white heat, or by reducing **chromic chloride** (Cr_2Cl_6) with sodium or zinc. In chromic salts the hexad radical Cr_2^{vi} exists, whilst in the higher oxides the single hexatomic atom Cr is alone present. Chromic salts are either green or violet in colour; those containing **chromic anhydride** (CrO_3) are yellow, orange, or red. Heated to redness in the air, it soon exhibits a yellowish-bluish tarnish like that seen upon steel under similar circumstances; this gradually changes to a thin film of green oxide. It rapidly dissolves in hydrochloric acid, evolving hydrogen, and forming blue **chromous chloride.** At ordinary temperatures dilute sulphuric acid does not interfere with it; but on the application of a gentle heat, an instantaneous and violent action occurs, leaving the remnant of the metal in a condition easily acted upon, even after washing, by the same acid in its weakest form. Nitric acid, in any degree of dilution or concentration, is quite powerless on chromium.

(*For detection, separation, and estimation of Chromium, see Author's* **Analytical Chemistry**, *pages* 39 *and* 172.)

Having thus reviewed the metals, it next becomes necessary to study the Metalloids, not only with regard to their individual properties, but as to their compounds *inter se* and with the metallic elements already considered.

CHAPTER IV.

FLUORINE AND CHLORINE.

CHEMICAL bodies have an official designation; but they are described by various titles, either popular, hereditary, or scientific. These different names, meaning the same thing, are called **synonyms**, and have in the following pages been invariably attached. The synonym is not strictly the translation of the word, but the mode in which it is expressed other than by the term used in accordance with its accepted present nomenclature.

FLUORINE. Symbol, F. Atomic Weight, 19. Atomicity, Monad.

Although the existence of this body is quite certain, it has not yet been isolated, owing to its powerful action on all vessels of glass and porcelain as well as of silver and platinum. It combines directly with all metals to produce fluorides, and has been stated to have been obtained as a gas something like chlorine by the action of perfectly dry iodine on argentic fluoride, but the experiment wants confirmation.

HYDROGEN FLUORIDE (SYN. *Hydrofluoric Acid*). **Formula, HF. Molecular Weight, 20.**

Is prepared by heating together **calcium fluoride** and **sulphuric acid** in a leaden vessel:—

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

The real acid is a gas, which when passed into water dissolves and forms a commercial liquid acid, containing 37 per cent. of real HF. Both this solution and the gas itself act with great avidity upon glass by combining with the silicic anhydride (silica) contained therein, and forming silicon tetrafluoride. It is therefore much used for etching the patterns on glass with which we are all familiar. In commerce the acid is occasionally stored in leaden bottles, but usually it is preserved in gutta percha. (*See* **Silicon.**)

CALCIUM FLUORIDE (SYNS. *Derbyshire Spar. Fluor Spar. Blue John*). **Formula, CaF_2. Molecular Weight, 78.**

Is found native in fine blue cubical crystals, but the colour is not always constant, varying through violet, yellow, rose, and even sometimes colourless. It is much used for glass etching. When employed for preparing the acid, leaden retorts and condensers must be used.

Compounds of fluorine are not employed in medicine or pharmacy.

(*For detection and separation of Hydrofluoric Acid and Fluorides, see Author's* **Analytical Chemistry**, *page* 49.)

CHLORINE (Syn. (obsolete) *Oxy-Muriatic Acid*). **Symbol, Cl_2. Atomic Weight, 35·5. Density,** *referred to Hydrogen*, **35·5. Density,** *referred to Air*, **2·46. Weight of a litre, 3·17 grammes** = **35·5** *criths*.* **Weight of 100 cubic inches, 76·3** *grains at* **60°** *F. and* **30** in. *barom.* **Atomicity, Monad.**

This element was discovered by Scheele in 1774. It does not exist free in nature, but is found chiefly in combination with sodium as common salt, which is the great natural reservoir for chlorine. It is also found combined with magnesium, silver, lead, and many other substances. In the vegetable kingdom it is not abundant; but chlorides are found in every secretion from animals. When persons are suffering from *pneumonia*, however, the absence of chlorides from the urine is a marked and curious symptom. It is prepared :—

1. By pouring **sulphuric acid** upon a mixture of **sodium chloride** and **manganic dioxide**. The action, which occurs at once, without the application of heat, is usually represented as follows :—

$$2NaCl + MnO_2 + 2H_2SO_4 = Cl_2 + Na_2SO_4 + MnSO_4 + 2H_2O.$$

In reality the action is probably much more complicated. The sulphuric acid first acts on the sodium chloride to produce hydrochloric acid :—

$$4NaCl + 2H_2SO_4 = 4HCl + 2Na_2SO_4.$$

The acid thus produced then acts upon the manganic dioxide to produce manganic tetrachloride :—

$$4HCl + MnO_2 = MnCl_4 + 2H_2O.$$

On heating slightly, this is decomposed thus :—

$$MnCl_4 = MnCl_2 + Cl_2.$$

The H_2SO_4 gives rise to a considerable amount of heat when it acts upon the NaCl, and the $MnCl_4$ is therefore decomposed as soon as it is formed.

2. By *heating* **hydrochloric acid** with **manganic dioxide** :—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

This is the preferable manner of preparing chlorine on a small scale, because the action only occurs when heat is actually applied, and the process is therefore well under control.

When this process is used on a manufacturing scale, the MnO_2 may be recovered by *Weldon's method*, as follows. The solution of $MnCl_2$ left in the retort is precipitated with lime, forming manganous oxide.

$$MnCl_2 + CaO = MnO + CaCl_2.$$

The precipitate is then mixed with some more lime, and air is blown through the whole, which causes the conversion of the MnO into MnO_2.

3. By passing mixed air and hydrochloric acid gas over heated fire-bricks previously soaked in a solution of copper and dried. Cuprous chloride is formed first, which takes up chlorine and becomes cupric chloride.

$$Cu_2Cl_2 + 2HCl + O = 2CuCl_2 + H_2O.$$

And then, by an increased heat, gives off the chlorine and re-forms cuprous chloride :—

$$2CuCl_2 = Cl_2 + Cu_2Cl_2,$$

which is ready for use again. This is known as *Deacon's process*, and gives chlorine containing the nitrogen of the air; but that is of no consequence for the manufacture of bleaching powder.

* One litre of hydrogen weighs 0·0896 gramme. A volume sometimes called a crith. A very small weight, usually a milligramme.

4. By heating magnesium chloride with manganese peroxide (*Macqueen's process*).

$$2MgCl_2 + MnO_2 = 2MgO + MnCl_2 + Cl_2$$

5. By heating hydrochloric acid with potassium dichromate.

$$K_2Cr_2O_7 + 14HCl = 3Cl_2 + 2KCl + Cr_2Cl_6 + 7H_2O.$$

6. By the electrolysis of hydrochloric acid.

$$2HCl = Cl_2 + H_2.$$

7. By fusing together ammonium chloride and ammonium nitrate.

$$2NH_4Cl + 4NH_4NO_3 = Cl_2 + 5N_2 + 12H_2O.$$

When chlorine is required free, it must be collected by displacement; that is, by passing the tube conveying the gas from the generating flask, to the bottom of a deep and dry bottle in which the chlorine gradually collects, displacing the air until the vessel is full. Thus obtained, it is observed to be a greenish yellow gas possessing a pungent and irritating odour, and proving instantly fatal to animal life, even when diluted with sixty times its bulk of air. Should it be accidentally inhaled, the best known antidote is ammonia gas.

Chlorine is much heavier than air, and is exceedingly soluble in water, which at ordinary temperatures dissolves 2½ times its volume. This solution is known as chlorine water, and possesses the property of dissolving gold, of liberating iodine and bromine from their salts, and of raising iron from the ferrous to the ferric state. When cooled to the freezing point, a solution of chlorine deposits crystals of chlorine hydrate ($Cl5H_2O$). It is possible to liquefy the gas by a pressure of four atmospheres, or about 64lbs. per square inch, but no attempts to solidify it have hitherto been successful.

Chlorine has an energetic action on metals, with which it combines directly to form chlorides. Powdered antimony, iron, and also magnesium and sodium, take fire when placed in a vessel of the gas, and even gold leaf slowly combines to form $AuCl_3$. The metalloids are also in many cases readily attacked; phosphorus and sulphur both burning in an atmosphere of chlorine to form chlorides, while selenium, silicon, and boron unite with it when heated; but it has no *direct* action upon either oxygen or carbon.

Compounds rich in hydrogen all unite readily with chlorine, forming hydrochloric acid, and setting carbon free if present. For example: (*a*) A piece of paper dipped in turpentine ($C_{10}H_{16}$) takes fire in a bottle of dry chlorine:—

$$C_{10}H_{16} + 8Cl_2 = C_{10} + 16HCl.$$

(*b*) Olefiant gas (C_2H_4) explodes with chlorine when a spark is applied, thus:—

$$C_2H_4 + 2Cl_2 = 4HCl + C_2.$$

Marsh gas (CH_4), however, does not liberate carbon; but, when mixed with excess of chlorine and exposed to sunlight, yields chloroform and carbon tetrachloride:

$$2CH_4 + 7Cl_2 = CHCl_3 + CCl_4 + 7HCl.$$

From its power of thus attracting hydrogen, chlorine can displace that element from many compounds to a greater or less extent. An example of this is found in the manufacture of chloral (C_2HCl_3O) by passing chlorine into alcohol (C_2H_5HO):—

$$C_2H_5HO + 4Cl_2 = C_2HCl_3O + 5HCl.$$

Chlorine acts as an indirect oxidizer by thus combining with hydrogen and liberating oxygen, and forms one of the most useful of disinfecting and deodorizing agents. It also performs the function of a bleacher of organic colouring matter, such as indigo and other vegetable dyes, *when moisture is*

present, by reason of a similar indirect oxidation, or by entering into combination with the pigment. For example: indigo (C_8H_5NO) is first oxidized to isatine ($C_8H_5NO_2$), and then converted into chlor-isatine ($C_8H_4ClNO_2$), thus:—

$$C_8H_5NO + Cl_2 + H_2O = C_8H_5NO_2 + 2HCl.$$
$$C_8H_5NO_2 + Cl_2 = C_8H_4ClNO_2 + HCl.$$

Liquor chlori of the B.P. is prepared by heating manganese peroxide with hydrochloric acid and passing the gas first through a little water to wash it, and then into a larger bulk of distilled water.

It is a yellowish-green liquid, smelling strongly of chlorine, and immediately discharging the colour of a dilute solution of sulphate of indigo. Specific gravity, 1·003. By exposure to light, it rapidly changes to hydrochloric acid, at the same time liberating oxygen:—

$$2Cl_2 + 2H_2O = 4HCl + O_2.$$

(*For detection of free Chlorine and analysis of Chlorine water, see Author's* **Analytical Chemistry**, *page* 49.)

When equal volumes of chlorine and hydrogen are mingled together, with the application of an electric spark, they combine to form hydrochloric acid.

$$\begin{array}{ccccc} Cl_2 & + & H_2 & = & 2HCl. \\ 2 \text{ vols.} & + & 2 \text{ vols.} & = & 4 \text{ vols.} \end{array}$$

The reaction occurs so readily that even exposure to a ray of sunlight causes an explosion.

METALLIC CHLORIDES.

HYDROGEN CHLORIDE (SYNS. **Hydrochloric Acid.** *Muriatic Acid. Spirit of Salt*). **Formula, HCl. Molecular Weight, 36·5. Density,** *referred to Hydrogen*, **18·25. Density,** *referred to Air*, **1·27.**

This body is really a gas, and is prepared by exploding equal volumes of chlorine and hydrogen in a tube over mercury. All the adjuncts must be perfectly dry for the success of the experiment, as the gas is very soluble in water, one gallon of which dissolves 460 of hydrochloric acid gas at an ordinary temperature. Although not hitherto solidified, it has been liquefied by a pressure of forty atmospheres. Theoretically, hydrochloric acid is produced whenever a substance containing hydrogen is brought into contact with free chlorine. For example, we may refer to the decomposition of chlorine water when exposed to sunlight, already shown; or to the following reaction of chlorine upon sulphuretted hydrogen:—

$$\begin{array}{ccccc} 2H_2S & + & 2Cl_2 & = & 4HCl + S_2 \\ 4 \text{ vols.} & + & 4 \text{ vols.} & = & 8 \text{ vols.} \end{array}$$

The *acidum hydrochloricum* of the B.P. is a solution of the gas in water to the extent of 31·8 per cent. It is prepared by heating a mixture of **sodium chloride** and **sulphuric acid**, then passing the evolved gas into cold **water**:—

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4.$$

The sulphuric acid, after slight dilution, is poured upon the sodium chloride in a large flask, and, heat being applied, the gas is first passed through a three-necked Woulff's bottle containing four ounces of water, and then into a large bulk of distilled water kept perfectly cold. Thus prepared, it is an almost colourless and strongly acid liquid, emitting white fumes possessing a pungent odour. Specific gravity, 1·16.

(*For analysis of B.P. Hydrochloric Acid, see Author's* **Analytical Chemistry**, *page* 82.)

Acidum hydrochloricum dilutum has a specific gravity of 1·052, and contains 10·50 per cent. of real acid. It is made by taking 8 fluid ounces of the strong acid, and adding water till the whole measures 26½ ounces at 60° Fahr.

Commercial hydrochloric acid is produced largely in the manufacture of sodium sulphate used for making sodium carbonate by Leblanc's process. (*See* **Carbonates.**) Usually it is of a yellowish colour, and stronger than the pure B.P. acid, as it is often found to contain 40 per cent. of HCl.

It is frequently contaminated with **free chlorine, ferric** and **stannic chlorides, sulphurous** and **sulphuric acids,** and **arsenious acid.** These impurities are removed by heating with a little **potassium chlorate** and, when the action has concluded, by the addition of a little **barium sulphide** and distillation into pure water so soon as all traces of sulphuretted hydrogen have disappeared. The potassium chlorate produces chlorine, and changes the sulphurous into the less volatile sulphuric acid:—

$$H_2SO_3 + Cl_2 + H_2O = H_2SO_4 + 2HCl,$$

Whilst the sulphuretted hydrogen, afterwards developed, decomposes any volatile arsenious chloride which might have been formed. The common acid may be converted into a fairly pure acid by dilution with water and redistillation. Hydrochloric acid acts upon metals with the exception of gold, platinum, silver, lead, mercury, and some others, forming chlorides, with the **evolution of hydrogen, thus:—**

$$Zn_2 + 4HCl = 2ZnCl_2 + 2H_2.$$

When pure and cold it is powerless against copper, and acts but slowly when heated and brought into contact with the finely powdered metal.

All **oxides** (except those of Ag and Hg_2) dissolve in this acid, producing a **chloride and water, thus:—**

$$CuO + 2HCl = CuCl_2 + H_2O.$$

While upon **peroxides,** such as those of manganese or lead, it acts by forming chlorides and evolving chlorine, heat being usually required at the commencement. With **barium peroxide,** in the presence of a freezing mixture, however, it forms **hydrogen peroxide** *or hydroxyl* (*see* **Oxygen**) and **barium chloride**:—

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

With the exception of the **argentic, mercurous,** and **plumbic** salts, all chlorides are soluble in cold water, and the latter dissolves in the boiling liquid. **Cuprous chloride** is likewise only slightly soluble. Some chlorides of metalloids, such as **phosphoric chlorides,** are at once decomposed by contact with **water:**

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

The **antimonious** and **bismuthous chlorides** are not so thoroughly decomposed by water, having only part of their chlorine displaced by oxygen, and forming insoluble **oxychlorides,** which precipitate, hydrochloric acid being at the same time produced in solution. For example:—

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

Magnesium, aluminium, and zinc chlorides are not decomposed by simple contact with water, but only when their solutions are attempted to be evaporated to dryness.

The chlorides of ammonium, zinc, iron, and antimony are volatilized by heat without decomposition. Potassium and sodium chlorides are also capable of volatilization, the former at a bright red, the latter at a white heat.

(*For detection, separation, and estimation of Chlorides, see Author's* **Analytical Chemistry,** *pages 48, 52, 53, 150, 176 and 177.*)

AMMONIUM CHLORIDE (Syn. *Sal-ammoniac*). **Formula, NH_4Cl. Molecular Weight, 53·5.**

This substance is prepared from the **ammoniacal liquors** of gas works, either by directly neutralizing with **hydrochloric acid**, or more commonly by first forming **ammonium sulphate** and subliming that salt with **sodium chloride**:—

$$(NH_4)_2SO_4 + 2NaCl = 2NH_4Cl + Na_2SO_4.$$

The B.P. describes it as follows:—

"In colourless, inodorous, translucent, fibrous masses; tough, and difficult to powder: soluble in water and in rectified spirit. When heated it volatilizes without decomposition and leaves no residue." As already noted in the chapter on theories, the vapour of this salt undergoes *dissociation* at a high temperature into HCl and NH_3, which again unite on cooling.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 82.)

Ammonium chloride is used in analysis to prevent the precipitation of magnesium hydrate by ammonium hydrate or ammonium carbonate. When heated with an alkaline hydrate, ammonia gas is evolved.

$$2NH_4Cl + Ca2HO = CaCl_2 + 2NH_3 + 2H_2O.$$

SODIUM CHLORIDE (Syns. *Common Salt. Table Salt*). **Formula, NaCl. Molecular Weight, 58·5.**

Occurs native in mines as *rock-salt*, and is also extracted from *sea water* by evaporation and crystallization. Referring to this useful substance, the B.P. says it should be in small, white, crystalline grains or transparent cubic crystals; free from moisture and having a purely saline taste.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 83.)

Common salt is soluble in three parts of cold water, and boiling water fails to increase its solubility to any marked extent. It is not soluble in pure alcohol, and but slightly in ordinary spirit. When exposed to a sudden increase of temperature, it *decrepitates*; the water mechanically imprisoned between its particles being rapidly converted into steam, and so creating an abrupt disruption of the crystals, accompanied by a loud crackling sound. When heated to bright redness it volatilizes in the most perceptible manner, and great caution is therefore required to keep the temperature low in the taking of the ash of substances, such as milk, in which it is intended to estimate the amount of salt.

POTASSIUM CHLORIDE. Formula, KCl. Molecular Weight, 74·5.

This substance is contained in sea and other mineral waters, and is extracted by evaporation. It also occurs native. Although only slightly soluble in rectified spirit, it dissolves with greater readiness, and to a larger extent, in distilled water than sodium chloride. It is also somewhat more volatile than the latter body.

ARGENTIC CHLORIDE (Syns. *Chloride of Silver. Horn Silver*). **Formula, AgCl. Molecular Weight, 143·5.**

Is formed as a curdy white precipitate when **argentic nitrate** is added to a solution of any **chloride**. It is readily soluble in **ammonium hydrate**, but resists the solvent effects of **nitric acid**; it is also soluble in **sodium hyposulphite** and **potassium cyanide**. Digested in potassium bromide, it yields argentic bromide, AgBr, and with potassium iodide it forms argentic iodide,

AgI. It is somewhat soluble in strong solutions of alkaline chlorides, especially in ammonium chloride.

CALCIUM CHLORIDE. Formula, $CaCl_2$. Molecular Weight, 111.

This substance, which on the manufacturing scale is a bye-product in the preparation of ammonia gas, is also produced by dissolving **calcium carbonate** in **hydrochloric acid.**

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

According to the B.P.,—

It may be formed by neutralizing hydrochloric acid with carbonate of lime, adding a little solution of chlorinated lime and slaked lime, filtering and evaporating until a solid residue is left, then drying the salt at about 400° F.

The reason for using chlorinated lime and slaked lime is that nearly all native calcium carbonate, even in a fairly pure form, as white marble, contains iron, and when the mineral is treated with hydrochloric acid it passes into solution chiefly as **ferrous chloride** ($FeCl_2$). The chlorine given off by the chlorinated lime in contact with the acid solution (*see* **Hypochlorites**) changes the **ferrous** into **ferric chloride**, and the **calcium hydrate** precipitates the iron as **ferric hydrate**, which being insoluble (*see* **Hydrates**), is easily removed, leaving a pure neutral solution of **calcium chloride** :—

$$4FeCl_2 + Ca2ClO + 4Ca2HO + 2H_2O = 5CaCl_2 + 2Fe_26HO.$$

Calcium chloride is usually met with in Pharmacy in white agglutinated masses, dry but very deliquescent. It can however also be crystallized in prisms having the formula $CaCl_26H_2O$. When dried *in vacuo* it becomes $CaCl_22H_2O$, and when strongly heated it loses its water of crystallization, and fuses. The fused mass stirred until it cools, and thus aggregated into lumps, is used in analysis for absorbing moisture and drying gases, because it is very deliquescent and is capable of absorbing even more water than is necessary to convert it into a liquid. When crystallized and dissolved in water it reduces the temperature considerably, and is therefore employed in the production of extreme cold. The fused chloride must not be used for this purpose, as it develops instead of absorbing heat when placed in contact with water, because it combines with it and takes up water of crystallization. Calcium chloride will not develop chlorine in contact with acids, and must not be confounded with the substance commonly called chloride of lime (*calx chlorata*, B.P.)

(*For analysis and impurities, see Author's* **Analytical Chemistry,** *page* 83.)

BARIUM CHLORIDE (SYN. (obsolete) *Muriate of Barytes*). **Formula, $BaCl_22H_2O$. Molecular Weight, 244.**

Is prepared by dissolving **barium carbonate** in **hydrochloric acid** :—

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O.$$

Or it may be made from **barium sulphate** by igniting it with coal to reduce it to **sulphide** :—

$$BaSO_4 + 2C_2 = BaS + 4CO,$$

And then dissolving the **barium sulphide** in **hydrochloric acid** :—

$$BaS + 2HCl = BaCl_2 + H_2S.$$

It forms crystals containing $2H_2O$, is soluble in water, nearly insoluble in alcohol, and its solution is used as a reagent for detecting and estimating **sulphuric acid**, with which it forms a precipitate of **barium sulphate** :—

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

MAGNESIUM CHLORIDE. Formula, $MgCl_2$. Molecular Weight, 95.

Is prepared in solution by dissolving **magnesium carbonate** in **hydrochloric acid.** This solution cannot be evaporated to dryness, as it deposits magnesium hydrate and the hydrochloric acid escapes; but if **ammonium chloride** be added, it forms magnesium-ammonium chloride, and when this is dried the ammonium chloride alone is driven off, leaving pure magnesium chloride behind. It is one of the most deliquescent substances known, and is used for the preparation of the metal magnesium.

ZINC CHLORIDE. Formula, $ZnCl_2$ Molecular Weight, 136.

Is prepared in an absolutely pure and anhydrous state by distilling perfectly dry **zinc sulphate** with **calcium chloride.** The B.P. salt, which contains some water of crystallization, is prepared by evaporating *liquor zinci chloridi* until it solidifies on cooling. It is employed as a caustic, and is described as being in colourless opaque rods or tablets, very deliquescent, and soluble in water, alcohol, and ether.

Liquor zinci chloridi is prepared by dissolving **zinc** in **hydrochloric acid.**

$$Zn_2 + 4HCl = 2ZnCl_2 + 2H_2.$$

Put 1 lb. of zinc into a porcelain basin, add by degrees 44 ounces of hydrochloric acid diluted with 20 ounces of water, and gently warm it on a sand bath until gas is no longer evolved. Boil for half an hour, and filter into a gallon bottle, add chlorine water until the fluid acquires a permanent odour of chlorine, and then add zinc carbonate with agitation, until a brown sediment appears. Filter and evaporate to a bulk of 2 pints.

The chlorine water and zinc carbonate are used to remove iron and lead, which are contained in nearly all commercial samples of metallic zinc. The **chlorine** changes the **iron** from the **ferrous** to the **ferric** state, and the **zinc carbonate** precipitates the iron as **ferric hydrate** and the lead as **peroxide.**

$$2FeCl_2 + PbCl_2 + 2Cl_2 + 5ZnCO_3 + 3H_2O = 5ZnCl_2 + Fe_2 6HO + PbO_2 + 5CO_2.$$

Zinc chloride constitutes Burnett's disinfecting and deodorizing fluid. It is an acrid, strongly acid substance, and a powerful poison. Any alkaline carbonate (as chalk or washing soda) will act as an antidote. It precipitates albumen and gelatin.

Zinc chloride has a burning taste, and can be sublimed with tolerable facility.

On account of its great affinity for water it may be substituted for sulphuric acid for preparing ether. A strong solution cannot be filtered, as it dissolves paper.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 83.)

CUPRIC CHLORIDE. $CuCl_2$ and

CUPROUS CHLORIDE. Cu_2Cl_2 *or* CuCl.

Result from the solution of cupric oxide, CuO, and cuprous oxide, Cu_2O, in hydrochloric acid. The cupric salt is green, the cuprous colourless. Neither are of pharmaceutical interest; but cupric chloride is very useful for the separation of citrates from tartrates (*see* **Citric Acid**), and a perfectly neutral solution is therefore a handy laboratory reagent. The cuprous chloride solution is used in volumetric analysis of gases for absorbing carbonic oxide.

MERCUROUS CHLORIDE (SYNS. *Calomel. Calomelas. Hydrargyri Subchloridum*). **Formula, HgCl** *or* **Hg_2Cl_2. Molecular Weight, 235·5** *or* **471.**

Is prepared by subliming together a mixture of **mercuric sulphate, metallic mercury,** and **sodium chloride.** The excess of mercury changes the mercuric sulphate to mercurous sulphate, thus :—

$$2HgSO_4 + Hg_2 = 2Hg_2SO_4.$$

And the sodium chloride then produces mercurous chloride by double decomposition, thus :—

$$Hg_2SO_4 + 2NaCl = Hg_2Cl_2 + Na_2SO_4 ;$$

Or the reaction may be represented in one equation, thus :—

$$HgSO_4 + Hg + 2NaCl = Hg_2Cl_2 + Na_2SO_4.$$

The mercuric sulphate is moistened, and rubbed with the mercury until globules are no longer visible. The sodium chloride is added, and the whole sublimed by a suitable apparatus into a chamber of such size that the calomel, instead of adhering to its sides as a crystalline crust, shall fall as a fine powder on its floor. This powder is washed with boiling water until the washings cease to be darkened by a drop of sulphide of ammonium, and finally dried at a heat not exceeding 212°. Thus prepared, calomel is a dull white, heavy, and nearly tasteless powder, rendered yellowish by trituration in a mortar; insoluble in water, spirit, or ether, and entirely volatile by heat.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 85.)

When treated with either **potassium, sodium,** or **calcium hydrate,** it becomes black, owing to the formation of **mercurous oxide.**

$$Hg_2Cl_2 + Ca2HO = CaCl_2 + Hg_2O + H_2O.$$

While with **ammonium hydrate** it yields a black variety of *hydrargyrum ammoniatum*, called **mercurous ammonium chloride** :

$$Hg_2Cl_2 + 2NH_4HO = NH_2Hg_2Cl + NH_4Cl + 2H_2O.$$

Lotio hydrargyri nigra is calomel treated with limewater, and therefore contains mercurous oxide suspended in a very weak solution of calcium chloride.

Owing to the cost of mercury, and the natural desire of the manufacturer to save expense, it sometimes happens that sufficient mercury is not added to cause all the mercuric sulphate to assume the mercurous state, and in this case the calomel is contaminated with mercuric chloride. This is a very dangerous thing, as will be seen when we consider that while we may give 5 grains of calomel for a dose, the outside dose of mercuric chloride is [illegible] of a grain ; and every conscientious pharmacist should always examine parcels of calomel. The test given in the B.P. is to shake with ether, and see if anything dissolves ; but a more simple and inexpensive method is to place the suspected calomel on a filter, and wash it once or twice with boiling distilled water. If mercuric chloride be present it will dissolve, and may be tested for in the filtrate with *liquor potassæ*, with which it gives a yellow precipitate.

Reducing agents, such as stannous chloride, cause mercurous chloride to be converted into metallic mercury. When subjected to the action of hydrocyanic acid, calomel is decomposed into mercuric chloride and metallic mercury ; the latter, in consequence of its finely divided state, possessing a blackish colour.

Mercurous chloride may also be produced by precipitating **mercurous nitrate** or **sulphate** with **hydrochloric acid**, or **sodium** and **ammonium chlorides**. Also by heating **mercuric chloride** with **mercury**, or reducing it by **sulphurous acid.**

MERCURIC CHLORIDE (SYNS. *Corrosive Sublimate. Bichloride of Mercury. Hydrargyri Perchloridum*). **Formula, $HgCl_2$. Molecular Weight, 271.**

Prepared by subliming **mercuric sulphate** with **sodium chloride**:—

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

Mercuric sulphate and the sodium chloride are mixed with a little manganese peroxide, and the mixture is put into an apparatus adapted for sublimation, and sufficient heat applied to cause vapours of perchloride of mercury to rise into the less heated part of the apparatus, which has been arranged for their condensation. The mercuric chloride collects in heavy, colourless masses of prismatic crystals, possessing a highly acrid metallic taste; more soluble in alcohol, and still more so in ether, than in water, and entirely volatile by heat.

The use of adding the manganic dioxide is to produce a little free chlorine, and so to prevent the formation of calomel.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 83.)

When treated with **potassium, sodium,** or **calcium hydrate**, it yields a yellow precipitate of **mercuric oxide**. Reducing agents, such as stannous chloride, change mercuric chloride first to calomel and finally to metallic mercury.

The precipitation of albuminous and fibrinous matters by this salt causes it to be employed as a preserver of animal textures, increasing their firmness, and entirely arresting the putrefactive process. In order that an aqueous solution of mercuric chloride may be obtained which is not liable to spontaneous decomposition, the B.P. directs that an equal quantity of ammonium chloride be simultaneously dissolved in the water. If this direction be not attended to, mercurous chloride may be formed, together with hydrochloric acid and oxygen gas; thus:—

$$4HgCl_2 + 2H_2O = 2Hg_2Cl_2 + 4HCl + O_2.$$

In the presence of ammonium chloride, the tendency of the mercuric chloride to form double salts being satisfied, this decomposition is averted. Upon litmus paper which has been reddened by mercuric chloride, sodium chloride exerts an alkaline action, restoring its blue colour.

AMMONIO MERCURIC CHLORIDE (SYNS. *Mercur-Ammonium Chloride. White Precipitate*). **Formula, NH_2HgCl. Molecular Weight, 251·5.**

Is produced when a solution of **mercuric chloride** is added to **ammonium hydrate**:—

$$HgCl_2 + 2NH_4HO = (NH_2Hg)Cl + NH_4Cl + 2H_2O.$$

In this reaction the dyad radical Hg'' displaces H_2' from the monad radical NH_4, and produces a radical which is called mercur-ammonium (NH_2Hg), which acts as a monad, and forms salts similar in formula to those of ammonium. The mercury may also entirely displace the hydrogen of the NH_4, giving rise to the radical called di-mercur-ammonium (NHg_2), acting as a monad; or a similar thing may take place with the double molecule of ammonium (N_2H_8), which may, by displacement of H_2 by mercury, become

mercur-di-ammonium (N_2H_6Hg), acting as a dyad radical and also forming salts. Thus we have :—

$(NH_4)Cl$.	$(NH_2Hg)Cl$.
Ammonium Chloride.	Mercur-ammonium Chloride.
$(NHg_2)Cl$.	$(N_2H_6Hg)Cl_2$.
Di-mercur-ammonium Chloride.	Mercur-di-ammonium Chloride.

As to mercur-ammonium chloride, which is called *hydrargyrum ammoniatum* in the B.P., that authority instructs us to dissolve the mercuric chloride in water and to add this solution to the ammonium hydrate, constantly stirring, to collect the precipitate on a filter, and wash it well with cold distilled water, and lastly, to dry the product at a temperature not exceeding 212°.

Thus prepared, hydrargyrum ammoniatum is an opaque white powder, on which cold water, alcohol, and ether have no action, and entirely volatile by heat.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 84.)

It is necessary to add the mercuric chloride to the ammonium hydrate, and wash, exactly as ordered, otherwise the colour of the substance would be rendered yellow, owing to the formation of hydrated di-mercur-ammonium chloride, $(NHg_2)ClH_2O$, which is produced either by boiling water, or even by the prolonged action of cold water.

The white precipitate of the B.P. *does not fuse* before volatilizing when heated. All parcels should be examined in this way, because it is not uncommon to have the mercur-di-ammonium chloride $(N_2H_6Hg)Cl_2$ substituted for the proper B.P. article. This is the old "*fusible white precipitate*" of the London Pharmacopœia 1824, and is prepared by precipitating mixed solutions of mercuric chloride and ammonium chloride by sodium carbonate. It contains less mercury than the B.P. precipitate, and *fuses before volatilizing* by heat. Other adulterations, such as white lead or chalk, are left as residues on volatilization.

AURIC CHLORIDE (SYNS. *Chloride of Gold. Terchloride of Gold*). **Formula, $AuCl_3$**, and

STANNIC CHLORIDE (SYNS. *Tetrachloride of Tin. Tin Liquor*. **Formula, $Sn^{iv}Cl_4$**.

May be produced by the solution of the respective metals in nitrohydrochloric acid. They are chiefly used for analytical purposes, the former is sometimes employed, either alone or in combination with potassium cyanide, for electro-plating. The last named ($SnCl_4$) is valuable to dyers.

ALUMINIUM CHLORIDE. Formula, Al_2Cl_6.

Interesting on account of its peculiar method of production, and being used in making the metal. It is produced when chlorine is passed over a mixture of aluminium oxide and carbon heated to redness.

$$Al_2O_3 + C_3 + 3Cl_2 = Al_2Cl_6 + 3CO.$$

The mixture of aluminium oxide and carbon, which must be very intimate, is made by mixing aluminium hydrate with oil and flour, and heating to redness.

A solution of aluminium chloride forms the so-called "*Chloralum*."

MANGANOUS and STANNOUS CHLORIDES. Formulæ, $MnCl_2$ *and* $SnCl_2$.

Can be obtained by boiling the metal or the hydrate with hydrochloric acid. The former may also be formed by treating any oxide of maganese with boiling hydrochloric acid.

Stannous chloride constitutes one of the most useful tests for mercury and for gold. With the former it yields a grey, and with the latter a black precipitate. In each case the precipitate consists of the respective metals in a finely divided state.

(*For analysis and impurities, see Author's* **Analytical Chemistry**; *page* 84.)

FERROUS CHLORIDE (SYN. *Chloride of Iron*). **Formula, $FeCl_2$. Molecular Weight, 127.**

Produced when **iron** is dissolved in **hydrochloric acid**:—

$$Fe_2 + 4HCl = 2FeCl_2 + 2H_2.$$

The greenish solution thus obtained, evaporated out of contact with the air, deposits greenish crystals of $FeCl_2 4H_2O$. Exposed to the air, it decomposes, changing partly to ferric chloride, and depositing a reddish-yellow ferric oxychloride.

FERRIC CHLORIDE (SYN. *Perchloride of Iron*). **Formula, Fe_2Cl_6. Molecular Weight, 325.**

Prepared in the anhydrous state by passing dry chlorine over iron filings heated to redness in a porcelain tube, terminated by a receiver in which the chloride collects. It is a red substance, appearing greenish by transmitted light, very volatile and deliquescent, and used occasionally in a solid state in pharmacy.

The *liquor ferri perchloridi fortior* of the B.P. is an acid solution of this substance, which is prepared by dissolving iron wire in hydrochloric acid; adding more hydrochloric acid, and a little nitric acid, and warming until the solution ceases to evolve red fumes, and becomes changed to a reddish-brown colour.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 84.)

By this method we first produce ferrous chloride by the action of iron wire and hydrochloric acid:—

$$3Fe_2 + 12HCl = 6FeCl_2 + 6H_2.$$

On heating this solution containing $FeCl_2$ with more hydrochloric acid and nitric acid, the latter becomes reduced to nitric oxide, and gives up nascent oxygen, which instantly combines with the hydrogen of the hydrochloric acid, and so liberates six atoms of chlorine to change the $6FeCl_2$ into $3Fe_2Cl_6$ (three molecules of ferric chloride) thus:

$$6FeCl_2 + 6HCl + 2HNO_3 = 3Fe_2Cl_6 + 2NO + 4H_2O.$$

Liquor ferri perchloridi is made by taking 5 fluid ounces of strong solution of perchloride of iron and 15 fluid ounces of distilled water, and mixing.

It is important for medical reasons in making this *liquor* not to exceed the quantity of acid, as the solution is to be taken internally; but for chemical reasons the acid is essential, because if too little HCl be used, a yellow deposit would form, very difficult to redissolve, and having the composition $Fe_2Cl_6 12Fe_2O_3$. The substance thus produced is therefore an oxychloride of iron, and is only one of the large series of very interesting compounds of a similar nature.

When *liquor ferri perchloridi* is digested with freshly precipitated ferric hydrate, the latter at once begins to dissolve, at first rapidly, but afterwards more slowly, until a point arrives at which the liquid becomes a jelly. This jelly is soluble in water, and is also an oxychloride containing from $Fe_2Cl_6 10Fe_2O_3$ to $Fe_2Cl_6 12Fe_2O_3$, according to the exact amount of ferric

hydrate dissolved. The solution of this jelly is not affected by boiling, dilution, or the addition of spirit, but it is instantly precipitated by the addition of a few drops of hydrochloric acid. By dialysis much of the crystalline ferric chloride may be removed from this compound, and the fluid remaining in the dialyzer is known as *liquor ferri dialysati*. (*See* **Ferric Hydrate.**)

A mixture of *liquor ferri perchloridi fortior* and rectified spirit constitutes *tinctura ferri perchloridi*, if the mixture be made in the proportion of three of spirit to one of the *liquor* by measure. The addition of the spirit, far from being an improvement, renders the mixture liable to deposit on keeping. In fact, it invariably produces an insoluble oxychloride, after a time varying with the season, and consequently with the temperature. Ethyl chloride and some other products are also simultaneously formed.

COBALTOUS CHLORIDE. Formula, $CoCl_2$, and

COBALTIC CHLORIDE. Formula, Co_2Cl_6.

Neither are of any interest from a pharmaceutical point of view. Both may be formed from the corresponding oxide by dissolving in cold hydrochloric acid. The former results from the action of this acid upon the metal also, and is red when hydrated but blue when anhydrous.

NICKELOUS CHLORIDE. Formula, $NiCl_2$.

When hydrated this salt is green, but when obtained anhydrous by sublimation is golden yellow. It may be produced by the action of chlorine on the heated metal, or by dissolving nickel oxide or hydrate in hydrochloric acid.

PLATINIC CHLORIDE (SYNS. *Perchloride of Platinum. Tetrachloride of Platinum.*) **Formula, $PtCl_4$.**

Is formed by dissolving the metal in nitro-hydrochloric acid. It requires some time to effect complete solution, and the whole is then evaporated to dryness on the water-bath with the addition from time to time of a little more hydrochloric acid, till all traces of nitric acid are expelled. The salt is thus obtained as a yellowish mass soluble in water, alcohol, and ether. When heated it fuses; and if a strong heat be applied it decomposes, leaving at first platinous chloride ($PtCl_2$), but afterwards nothing but metallic platinum remains. Platinic chloride is used for the quantitative estimation of potassium and ammonium, with which it forms insoluble double chlorides having the respective formulæ of $PtCl_4 2KCl$ and $PtCl_4 2NH_4Cl$.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 84.)

PLUMBIC CHLORIDE (SYNS. *Magistery of Lead. Horn Lead*). **Formula, $PbCl_2$**

The precipitate produced when a soluble salt of lead is mixed with hydrochloric acid. It is nearly insoluble in cold water, quite soluble in boiling water, and absolutely insoluble in alcohol. It may be prepared, though with difficulty, by boiling lead with very strong hydrochloric acid. 135 parts of cold water are required to dissolve it, but only 30 parts of boiling water are required.

ANTIMONIOUS CHLORIDE (SYN. *Liquor Antimonii Chloridi. Butter of Antimony.*) **Formula, $SbCl_3$.**

May be prepared solid as a transparent, colourless, fatty-looking mass,

which fumes slightly, and melts at 160° F., by distilling the B.P. *liquor antimonii chloridi*, until (the water and excess of acid having passed off) the product solidifies in the receiver.

The B.P. *liquor* is produced by dissolving the black native **sulphide of antimony** in strong boiling **hydrochloric acid**; cold acid being devoid of action.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The sulphide dissolves with the evolution of sulphuretted hydrogen gas, and leaves a solution of antimonious chloride in excess of undecomposed hydrochloric acid.

Liquor antimonii chloridi is a heavy liquid, usually of a yellowish-red colour, having a specific gravity of 1·47; when it is poured into water it forms a white precipitate of oxychloride of antimony, which has been found to contain $(SbCl_3)_2 5Sb_2O_3$; thus:—

$$12SbCl_3 + 15H_2O = (SbCl_3)_2 5Sb_2O_3 + 30HCl.$$

(*For analysis and impurities, see Author's* **Analytical Chemistry**, page 85.)

This substance was formerly used in medicine, and called the *powder of algaroth*, but its only interest now arises from its production in the course of making the B.P. *antimonii oxidum*. This precipitate is entirely soluble in tartaric acid, which serves to distinguish it from the similar oxysalts produced by acid solutions of bismuth, when diluted with water.

The colour of antimonious chloride is due, in most cases, to the presence of ferric chloride produced by the iron usually existing in the native antimonious sulphide employed. Sometimes, however, in consequence of an idea that the strength of the colour is an indication of the quality, this is *purposely* increased in depth by the addition of ferric nitrate.

BISMUTHOUS CHLORIDE, $BiCl_3$, and

OXYCHLORIDE, BiOCl.

The former is soluble in acidulated water, and the latter is produced as a white precipitate, on diluting a solution of the former extensively with water. The $BiCl_3$ is formed by the solution of the metal in hydrochloric acid. Bismuth oxychloride is a heavy white powder which is sometimes termed *bismuthyl chloride*, and is extensively used as a cosmetic under the name of *blanc des perles*. By ignition it is converted into the oxide.

CHROMOUS CHLORIDE, $CrCl_2$;

CHROMIC CHLORIDE, Cr_2Cl_6; and

PERCHROMIC CHLORIDE, $CrCl_6$.

The latter is not known in the free state, but is probably united with chromic anhydride, CrO_3, in chlorochromic anhydride, CrO_2Cl_2 or

$$2CrO_3.\ CrCl_6 = (Cr_3Cl_6O_6).$$

The chromous chloride results from the action of chlorine upon chromic oxide (Cr_2O_3) and carbon heated to redness.

Chromic chloride is produced by the same means; the chlorine, however, being passed over the mixture for a much longer time. It may be obtained in a hydrated form by dissolving chromic hydrate in hydrochloric acid, or by exposing the blue solution of chromous chloride to the air. The hydrated Cr_2Cl_6 decomposes, like magnesium chloride, by evaporation, depositing $Cr_2 6HO$ (chromic hydrate).

A solution containing perchromic chloride may be obtained, by acting on plumbic chromate with hydrochloric acid, which possesses the power of dissolving gold.

COMPOUNDS OF CHLORINE WITH OXYGEN.

Chlorine forms a series of oxides which yield their corresponding acids by the addition of H_2O, as follows :—

Hypochlorous Anhydride, Cl_2O.	**Hypochlorous Acid,** $HClO$.
Chloric Oxide (*undiscovered*), Cl_2O_2.	
Chlorous Anhydride, Cl_2O_3	**Chlorous Acid,** $HClO_2$.
Perchloric Oxide, or Chloric Peroxide, Cl_2O_4	
Chloric Anhydride (*undiscovered*), Cl_2O_5 . .	**Chloric Acid,** $HClO_3$.
Perchloric Anhydride (*undiscovered*), Cl_2O_7 .	**Perchloric Acid,** $HClO_4$.

HYPOCHLOROUS ANHYDRIDE. Formula, Cl_2O.

Is a yellowish gas with an irritating odour recalling that of chlorine. It is condensable by cold to a blood-red liquid, and is prepared by passing perfectly dry chlorine over *precipitated* and dried mercuric oxide, in a tube cooled to the freezing point :—

$$HgO + 2Cl_2 = Cl_2O + HgCl_2.$$

It is remarkable that the B.P. red mercuric oxide prepared from the nitrate will not thus act with chlorine.

In contact with water it should form hypochlorous acid :—

$$Cl_2O + H_2O = 2HClO.$$

In practice, however, no such action occurs.

HYDROGEN HYPOCHLORITE (SYN. *Hypochlorous Acid*).

May be prepared by passing chlorine into water containing calcium carbonate in suspension.

$$CaCO_3 + H_2O + 2Cl_2 = 2HClO + CaCl_2 + CO_2.$$

Also by passing air saturated with hydrochloric acid gas through a solution of potassium permanganate acidulated with hydrochloric acid and heated to 212° F., when HClO distils over.

(*For characters and detection, see Author's* **Analytical Chemistry**, page 50.)

This acid, in solution, as we prepare it, is a yellowish liquid, possessing in a concentrated degree the odour as well as the bleaching and oxidizing properties of chlorine. Treated with hydrochloric acid it is decomposed, forming chlorine and water :—

$$HClO + HCl = Cl_2 + H_2O.$$

It combines with metals to produce a class of salts called "hypochlorites," in which ClO acts as a monad acidulous radical. They are not employed in the pure state in Pharmacy, but occur mixed with chlorides under the names of *calx chlorata* and *soda chlorata*.

METALLIC HYPOCHLORITES.

SODA CHLORATA (Syns. *Chlorinated Soda. Labarraque's Liquid*). **Formula, NaClNaClO.**

Is prepared in solution as *liquor sodæ chloratæ* by passing chlorine gas into cold solution of sodium carbonate :—

$$Na_2CO_3 + Cl_2 = NaCl.NaClO + CO_2.$$

The B.P. instructs that the chlorine, prepared by heating hydrochloric acid with manganese peroxide, shall be passed into such an amount of sodium carbonate in solution that an excess of the latter shall be left unsaturated. The carbonic anhydride liberated acts upon this excess and converts it into sodium hydrocarbonate; and therefore the *liquor* really contains sodium hypochlorite, sodium chloride, and sodium hydrocarbonate, thus :—

$$2Na_2CO_3 + Cl_2 + H_2O = NaCl.NaClO + 2NaHCO_3.$$

Thus prepared it is an alkaline colourless liquid, smelling of chlorine and having a specific gravity of 1·103. It decomposes slowly at ordinary temperatures and rapidly on boiling, forming a mixture of sodium chloride and chlorate.

(*For analysis and impurities and volumetric estimation, see Author's* **Analytical Chemistry**, *pages* 85 *and* 158.)

CALX CHLORATA Syns. *Chlorinated Lime. Chloride of Lime. Bleaching Powder. Calcyl Chloride*). **Formula, $CaCl_2Ca2ClO$.**

Is prepared by passing chlorine gas over calcium hydrate. This most important industrial process is conducted by very carefully slaking the calcium oxide (which should be as free from magnesium and metals as possible, lest deliquescent magnesium chloride be formed, and the product be too much inclined to dampness), and rubbing it through a sieve until perfectly powdered. The powder is then spread out on shelves in a rectangular chamber, and the latter having been closed, chlorine gas is admitted at the top, and its passage continued as long as absorption takes place, and until a product has been formed which contains 33 per cent. of available chlorine. In winter this point is easily attained, but in summer it is not always possible, owing to the heat, which prevents full absorption.

Commercial *chloride of lime* is a dull white dampish powder smelling strongly of chlorine. It contains calcium hypochlorite, calcium chloride, calcium hydrate, and calcium carbonate, with sundry impurities. Water partially dissolves it, taking up the hypochlorite, chloride, and a little of the calcium hydrate, and leaving the bulk of the latter, together with the carbonate, etc., insoluble.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *pages* 85 *and* 158.)

Both the *soda* and *calx chlorata* evolve hypochlorous acid under the influence of very dilute acids, and even when simply in contact with the carbonic acid of the atmosphere. With the very slightest excess of any acid, such as sulphuric, however, they do not evolve that substance, but are decomposed, yielding chlorine :—

$$CaCl_2.Ca2ClO + 2H_2SO_4 = 2CaSO_4 + 2Cl_2 + 2H_2O.$$

This occurs, more strictly speaking, as follows :—

1. $CaCl_2.Ca2ClO + 2H_2SO_4 = 2CaSO_4 + 2HClO + 2HCl.$
2. $2HClO + 2HCl = 2Cl_2 + 2H_2O.$

By the last reaction, it is evident, that in the presence of hydrochloric acid, chlorine is also evolved.

$$CaCl_2.Ca2ClO + 4HCl = 2Cl_2 + 2CaCl_2 + 2H_2O.$$

The estimation of the amount of chlorine which any particular sample ot *bleaching powder* will evolve for industrial or other purposes is a matter of much importance. The chlorine thus estimated is called by the analyst *available chlorine*, and it is always ascertained by volumetric analysis.

(*See Author's* **Analytical Chemistry**, *page* 158.)

As it is impossible to demonstrate conclusively the existence of metallic chlorides in good chlorinated lime and soda, many chemists consider these products to be chlorides of the hypothetical radicals,—

Calcyl (CaO) and sodyl (Na_2O).

Thus :—

Sodyl Chloride, Na_2OCl_2.
Calcyl Chloride, $CaOCl_2$.

These formulæ may be accounted for, thus :—

$$Na—Cl_2—O—Na.$$
$$Cl—Ca—O—Cl.$$

In the sodium compound the group Cl_2 acts as a dyad, though it is usually a saturated molecule. If the calcium compound had the formula it is usually supposed to have, the calcium chloride could be dissolved by alcohol. As this cannot be done there seems no better explanation than to ascribe to the *calx chlorata* the above given composition.

CHLOROUS ANHYDRIDE (SYN. *Chlorous oxide*). **Formula, Cl_2O_3.**

Is a greenish yellow gas, only liquefiable by the most intense cold. It is prepared by heating a mixture of potassium chlorate with nitric and arsenious acids. The latter acid reduces the former to nitrous acid, which in its turn deoxidizes the chlorate. The action of the nitrous acid may be shown thus:—

$$2KClO_3 + 2HNO_2 = Cl_2O_3 + H_2O + 2KNO_3.$$

HYDROGEN CHLORITE (SYN. *Chlorous Acid*). **Formula, $HClO_2$.**

When chlorous anhydride dissolves in water this acid is formed, which combines with metals to form a class of salts called *chlorites*, which are of no pharmaceutical interest. It possesses bleaching properties, is a greenish liquid, and combines violently with alkaline hydrates.

A remarkable fact about chlorous acid is that it is destitute of the power of decomposing a carbonate.

PERCHLORIC OXIDE. Formula $Cl_2O_4 = 2ClO_2$.

A very heavy and exceedingly explosive yellow gas, produced by the action of strong sulphuric acid upon potassium chlorate :—

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + Cl_2O_4 + H_2O.$$

The least elevation of temperature, or the presence of any combustible or organic matter, instantly causes this gas to decompose, with a powerful explosion, into chlorine and oxygen. It can be condensed by cold into a liquid; and is the active agent in the well-known experiment of spontaneous combustion when a mixture of sugar and potassium chlorate is touched with strong sulphuric acid. It cannot be collected either over water or mercury, as it is decomposed by both.

By the action of the former perchloric oxide is decomposed into a mixture of chlorous and chloric acids :—

$$Cl_2O_4 + H_2O = HClO_2 + HClO_3.$$

HYDROGEN CHLORATE (Syn. *Chloric Acid*). **Formula, $HClO_3$.**

May be prepared in solution by the action of *very dilute* sulphuric acid upon a chlorate. The best one to use for this purpose is barium chlorate, because the bye-product of barium sulphate, being insoluble, can be easily removed by filtration.

$$Ba2ClO_3 + H_2SO_4 = 2HClO_3 + BaSO_4.$$

Thus prepared, and concentrated by evaporation *in vacuo*, it is a thick liquid, with an irritating chlorine-like odour, and immediately decomposed by organic matters or by heat. It combines with metals to form a class of salts, called *chlorates*, having for their acidulous radicals the group ClO_3, which acts as a monad. All **chlorates** are more or less soluble in water and decomposed by strong sulphuric acid.

Alkaline chlorates are prepared by passing chlorine into a solution of an alkaline hydrate, thus forming hypochlorite and chloride (already studied).

$$6KHO + 3Cl_2 = 3KClO + 3KCl + 3H_2O.$$

On boiling this solution, it decomposes, and forms a mixture of chloride and chlorate. The latter can be separated by fractional crystallization :—

$$3KClO + 3KCl = 5KCl + KClO_3.$$

Thus we see that the result of passing chlorine into a solution of an alkali, and heating, is the production of an *ide* and an *ate* in the proportion of five of the former to one of the latter.

This is an important fact to keep in mind, because it applies equally to iodine and bromine, and will assist materially in writing out equations.

(*For detection and separation of Chlorates, see Author's* **Analytical Chemistry**, *page* 50.)

POTASSIUM CHLORATE (Syn. *Chlorate of Potash*). **Formula, $KClO_3$. Molecular Weight, 122·5.**

Can be prepared as just described; but such a process would be very expensive, owing to the amount of potassium wasted as chloride. It has been found, however, that by substituting a proper proportion of slaked lime for $\frac{5}{6}$ of the potassium hydrate, all the former will become chloride while the latter only will form chlorate. By this process a great saving of potassium is effected ; and not only so, but as potassium hydrate is produced by potassium carbonate and slaked lime, it is only necessary to use 6 molecules instead of 5 of the latter, and then potassium carbonate can be employed. The B.P. process is therefore essentially to pass chlorine into a solution of potassium carbonate, mixed with slaked lime, until absorption ceases, boil the solution, filter, and crystallize. Viewed by the light of these explanations, an apparently very difficult equation becomes simple :—

$$K_2CO_3 + 6Ca2HO + 6Cl_2 = 2KClO_3 + 5CaCl_2 + CaCO_3 + 6H_2O.$$

In practice the lime and potassium carbonate are made into a paste with water, placed in a carboy, and chlorine passed through. The whole is then boiled with a good quantity of water, filtered, and crystallized.

The completion of the action of the chlorine is determined by examining the colour of the pasty mass in the carboy. If it be pink (owing to the formation of a small quantity of an alkaline permanganate from the trace of manganese mechanically carried over with the current of chlorine) no further

absorption will take place. Potassium chlorate is in colourless rhomboidal crystalline plates, sparingly soluble in cold water and insoluble in alcohol. It is much employed, either alone or mixed with hydrochloric or sulphuric acid, as an oxidizing agent. When heated in contact with organic substances, it speedily converts them into their ultimate products of combustion, viz., carbonic acid gas, water, and ammonia gas or nitrogen. In combination with hydrochloric acid it is used in toxicological investigations, for the purpose of destroying, to a considerable extent, such substances as might interfere with the detection of poisons. It was formerly supposed that potassium chlorate, when medicinally administered, tended to oxidize all the impurities with which it might come in contact; but it has been found that, like other saline bodies, it passes through the body with but little if any decomposition or alteration.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 85.)

Potassium and all alkaline chlorates yield oxygen when heated, and leave a residue of chloride :—

$$2KClO_3 = 2KCl + 3O_2.$$

While, on the other hand, chlorates of earthy and heavy metals evolve oxygen and chlorine, leaving oxides :—

$$2(Mg2ClO_3) = 2MgO + 2Cl_2 + 5O_2.$$

When potassium chlorate is heated until it fuses thoroughly, and begins to thicken, and the source of heat is withdrawn, a residue is left, containing potassium perchlorate together with potassium chloride.

$$2KClO_3 = KClO_4 + KCl + O_2.$$

A similar action takes place when potassium chlorate is treated with nitric acid ; only in this case the bye-product is nitrate instead of chloride :—

$$6KClO_3 + 4HNO_3 = 2KClO_4 + 4KNO_3 + 4O_2 + 2Cl_2 + 2H_2O.$$

The perchlorate obtained by either of these processes, being much less soluble in water than either of the bye-products, crystallizes out first.

PERCHLORIC ACID. Formula, $HClO_4$.

May be produced by distilling potassium perchlorate with sulphuric acid. It is a heavy colourless liquid, which, even when preserved in the dark, suddenly decomposes with explosion after a week or two. It explodes at once with fearful violence on touching organic matter or carbon.

POTASSIUM PERCHLORATE (SYN. *Perchlorate of Potash*). **Formula, $KClO_4$.**

May be obtained mixed with potassium nitrate by dropping crystals of potassium chlorate (one or two only at a time) into hot nitric acid, and afterwards separating by fractional crystallization. Explosion in this process is avoided because, instead of forming perchloric oxide, the chlorine and oxygen are liberated as a *mixture*, and not a compound. It is, like the chlorate, only slightly soluble in water. The perchlorates are not of pharmaceutical interest.

(*For detection of Perchlorates, see Author's* **Analytical Chemistry**, *page* 50.)

EUCHLORINE. Formula, $Cl_{12}O_6$.

This peculiar body, discovered by Sir Humphrey Davy, is a greenish-yellow gas, produced by the action of hydrochloric acid upon potassium chlorate. Its odour is characteristic, and it is a mixture of nine parts of chlorine and three of perchloric oxide :—

$$(3ClO_2 + 9Cl) = Cl_{12}O_6.$$
$$4KClO_3 + 12HCl = Cl_{12}O_6 + 4KCl + 6H_2O.$$

CHAPTER V.

BROMINE AND IODINE.

BROMINE.

BROMINE. Symbol, Br. Atomic Weight, 80. In the free state, Br_2 Molecular Weight, 160. Density of Vapour, *referred to Air*, **5·54. Density of Vapour,** *referred to Hydrogen*, **80. Atomicity, Monad.**

Exists in nature in certain saline springs, notably those near Kreuznach, in Germany. It is also found in sea water, in the state of magnesium bromide, and in the mother-liquors of kelp, along with iodine. (*See* **Iodine.**) The water of the spring is evaporated and crystallized, this process being repeated until all the alkaline chlorides and sulphates are removed.

The mother-liquor, which contains the magnesium bromide, is evaporated, and distilled with manganic dioxide and sulphuric acid. The neck of the retort is plunged under cold water, and the bromine collects in drops at the bottom.

$$MgBr_2 + MnO_2 + 2H_2SO_4 = Br_2 + MgSO_4 + MnSO_4 + 2H_2O.$$

The crude bromine thus obtained is finally rectified over calcium chloride. It is also prepared from the residual liquors of kelp, after removal of the iodine as cuprous iodide (*see* **Iodine**), by evaporation and distillation as above described.

Bromine is a dark brownish-red, very volatile liquid, with a strong and disagreeable odour. Its specific gravity is 2·966.

It is soluble in water to the extent of about 31 in 1000, the solution thus obtained having a specific gravity of 1·024. This solution is of a slightly orange colour, is not nearly so rapidly decomposed by light as chlorine water, and when cooled to the freezing point it forms, like chlorine, a definite solid hydrate, $Br5H_2O$. It is more soluble in alcohol than in water, and very freely so in ether, chloroform, and carbon disulphide, its solutions in these *menstrua* having a very characteristic yellowish-red tinge. Like chlorine, it acts as an indirect oxidant in contact with water; but is weaker in its affinities to basylous radicals than that substance, although stronger than iodine. Thus, while free chlorine will replace both bromine and iodine from a metal, free bromine will only displace iodine. It is, therefore, intermediate, in all its properties, between those two metalloids. The following table will give an idea of the relative powers of Cl, Br, and I, which constitute a group by themselves, under the name of *the Halogens*. They are thus called because they can combine directly with bases, without forming acids.

	Atomic Weight.	Character at Ordinary Temperature.	Behaviour of Solution in Light.
Cl	35·5	Gaseous	rapidly decomposed.
Br	80	Liquid	slowly ditto.
I	127	Solid	scarcely affected.

...mine is slightly volatile at ordinary temperatures, giving red vapours ... an exceedingly offensive odour; and heated to about 120° F., it boils, ... a vapour which has a density of 5·54 (referred to hydrogen, of 80), at ... it is converted into a reddish crystalline solid. Free bromine combines ... starch paste to form an orange red compound called bromide of starch, ... is not readily bleached by excess of chlorine.

(For detection of Bromine, see Author's **Analytical Chemistry**, *page* 51.)

METALLIC BROMIDES.

...DROGEN BROMIDE (SYN. *Hydrobromic Acid*). **Formula, HBr. Molecular Weight, 81.**

...s given off as a colourless gas, with a decided pungency, similar to that of ...rochloric acid, whenever **sulphuric acid** is heated with **potassium bromide** ...any alkaline bromide.

$$2KBr + H_2SO_4 = 2HBr + K_2SO_4.$$

It cannot be prepared thus in practice, because it is at once decomposed ... any **excess of sulphuric acid**, yielding **sulphurous anhydride** and free ...**omine**:

$$H_2SO_4 + 2HBr = Br_2 + SO_2 + 2H_2O.$$

It is therefore prepared in solution (1) by passing **sulphuretted hydrogen** ...rough **bromine** suspended in **water**:—

$$2H_2S + 2Br_2 = 4HBr + S_2;$$

... (2) by acting on **phosphorous bromide** with **water**, thus:

$$PBr_3 + 3H_2O = 3HBr + H_3PO_3.$$

This solution is very similar in appearance to ordinary aqueous HCl. Hydrogen **will unite with bromine vapour directly, to form this acid, but not** nearly so rapidly as in the case of chlorine, which acts by mere sunlight (as already mentioned), while bromine requires the application of a decided source of heat, and immediate contact therewith:—

$$\begin{array}{ccccc} Br_2 & + & H_2 & = & 2HBr. \\ 2 \text{ vols.} & + & 2 \text{ vols.} & = & 4 \text{ vols.} \end{array}$$

One gallon of bromine vapour thus requires one gallon of hydrogen to form two gallons of HBr.

Bromides are derived by the displacement of hydrogen from hydrobromic acid by a basylous radical. They are mostly soluble in water, except the argentic, mercurous, and plumbic salts.

(For detection, separation, and estimation of HBr and Bromides, see Author's **Analytical Chemistry**, *pages* 51, 53, 156, *and* 176.)

AMMONIUM BROMIDE (SYN. *Ammonii Bromidum*). **Formula, NH_4Br. Molecular Weight, 98.**

Sometimes prepared by the direct combination of **ammonium hydrate** and **hydrobromic** acid, but more commonly by mixing solutions of **ferrous bromide** and **ammonium carbonate.**

This latter precipitates ferrous carbonate, leaving the ammonium bromide in solution.

$$FeBr_2 + (NH_4)_2CO_3 = 2NH_4Br + FeCO_3.$$

The B.P. describes it as being in colourless crystals, which become slightly

yellow by exposure to the air, and have a pungent saline taste. Ammonium bromide may be sublimed unchanged by the application of heat. It is readily soluble in water, and less soluble in spirit.

(*For analysis and estimation, see Author's* **Analytical Chemistry,** *pages* 88 *and* 156.)

POTASSIUM BROMIDE (SYN. *Potassii Bromidum*). **Formula, KBr. Molecular Weight, 119.**

Prepared by dissolving **bromine** in heated solution of **potassium hydrate,** thus forming a mixture of potassium bromide and bromate:—

$$6KHO + 3Br_2 = 5KBr + KBrO_3 + 3H_2O.$$

The solution having been evaporated to dryness, the residue is heated in a crucible with a little charcoal, to change the bromate into bromide:—

$$KBrO_3 + C_3 = KBr + 3CO.$$

Potassium bromide is usually met with in transparent, cubical crystals with no odour, but a pungent saline taste; readily soluble in water, less soluble in spirit.

Potassium bromide is fusible by heat, and may be volatilized at a temperature not far removed from that necessary to vaporize potassium chloride. Like sodium chloride, heat causes it to decrepitate.

(*For analysis and impurities, see Author's* **Analytical Chemistry,** *page* 87.)

ARGENTIC BROMIDE (SYN. *Bromide of Silver*). **Formula, AgBr. Molecular Weight, 188.**

The dirty-white precipitate produced by **argentic nitrate,** in a solution containing a **bromide.** Insoluble in dilute nitric acid, but slowly soluble in *liquor ammoniæ.* Treated with free chlorine it gives up its bromine, and becomes argentic chloride. Digested for some time with potassium iodide it becomes argentic iodide.

FERROUS BROMIDE (SYN. *Bromide of Iron*). **Formula, $FeBr_2$. Molecular Weight, 216.**

May be produced by direct combination of **iron wire** and **bromine,** in the presence of water. (*See* **Ferrous Iodide.**)

COMPOUNDS OF BROMINE WITH OXYGEN.

Only two of these compounds are known (1) **Hypobromous Acid.** HBrO. corresponding to hypochlorous acid (*for detection, see Author's* **Analytical Chemistry,** *page* 51), and (2):—

HYDROGEN BROMATE (SYN. *Bromic Acid*). **Formula, $HBrO_3$.**

This acid may be obtained by acting on barium bromate with very dilute sulphuric acid. It closely resembles chloric acid, and forms salts called bromates, produced, as already seen, along with the corresponding bromide by the action of alkalies upon bromine. If desired, the bromate may be separated from the bromide by fractional crystallization, the former being much less soluble in water than the latter.

(*For detection of bromates, see Author's* **Analytical Chemistry,** *page* 52.)

IODINE.

IODINE. Symbol, I. Atomic Weight, 127. Vapour Density, ***referred to Hydrogen*****, 127. Vapour Density,** ***referred to Air*****, 8·71 In the free state, I_2. Molecular Weight, 254. Atomicity, Monad.**

Exists in sea water, and is stored up in the substance of many marine plants and animals. Cod-liver oil contains a decided percentage of iodine, and so do sponges. It is also found in many minerals, notably in rock-salt, and in the native saltpetre from Chili. In practice, it is chiefly extracted from certain varieties of *Algæ*, the most highly iodized variety being the *Fucus palmatus.* The seaweed is collected on the shore, dried, and placed in pits surrounded by a low wall. In these it is set on fire, when all the vegetable matter burns off, and the ashes are found at the bottom as a fused mass, which on cooling sets into a cake, and is called *kelp*.

There are two varieties of this ash; viz., drift seaweed kelp and cut seaweed kelp, the former being the richer in iodine.

The kelp is first digested in water in large vats, called *chests*, and the soluble parts having been thus extracted, the liquor is drawn off and evaporated in boilers. During this evaporation, sodium sulphate separates; and the liquid, on cooling, also deposits crystals of potassium chloride. This process is repeated until no more crystals can be obtained, and the uncrystallizable mother-liquor is then used for the production of iodine. It is called the *residual kelp liquor*, and contains the iodine as sodium iodide, together with carbonates and sulphides. The residual liquor is first neutralized with sulphuric acid, which causes a copious evolution of gases (CO_2, H_2S, and SO_2); and it is then boiled and cooled, when some more sodium sulphate is deposited, mixed with sulphur. The clear liquor is now run off into a still, and having been mixed with excess of sulphuric acid and manganic dioxide, heat is applied, when the iodine distils over in magnificent violet-coloured vapours, and collects in the receiver, leaving sodium and manganous sulphates [illegible]tort:—

$$2NaI + MnO_2 + 2H_2SO_4 = I_2 + Na_2SO_4 + MnSO_4 + 2H_2O.$$

The following statement relative to the practical results of this importan industry may be accepted as a record of practical experience.

	One Ton of Drift Weed Kelp yields:		One Ton of Cut Weed Kelp yields:	
	cwt.	*lbs.*	*cwt.*	*lbs.*
Iodine	0	12	0	2½
Potassium Chloride	4	84	3	56
Potassium Sulphate	2	84	3	56
Fished Salt*	2	84	3	56
Refuse Sulphur	0	28	0	56

This process with manganese and sulphuric acid, yields iodine contaminated with bromine, should that element be present in the kelp. It also produces chlorine from any of the chlorides in the liquor.

The production of chlorine is often apt to cause a loss of iodine by forming iodic chloride, ICl_3. It is, therefore, desirable to have a process by which the iodine can be separated from both these elements. This is attained by precipitating the purified residual liquor with a solution containing 1 part

* Trade name for other residual mixed salts.

cupric sulphate to 2·25 parts ferrous sulphate, when the iodine is precipitated as cuprous iodide, leaving the bromides and chlorides unaffected :—

$$2NaI + 2CuSO_4 + 2FeSO_4 = 2CuI + Na_2SO_4 + Fe_2 3SO_4.$$

The precipitated pure cuprous iodide is then collected, washed, and distilled with manganic dioxide and sulphuric acid, when perfectly pure iodine is obtained. After this separation, bromine may be obtained from the filtrate in very rich kelps.

A similar process has been recommended in analysis for detecting a bromide in presence of an iodide, but it is not sufficiently delicate for that purpose. Some trace of iodine invariably remains in solution, which, in the hands of the inexperienced, is forthwith mistaken for bromine.

Iodine is usually met with in laminar crystals, of a peculiar odour, black colour, and metallic lustre, which are entirely volatile by heat to a purple vapour. Its specific gravity is 4·948, and the density of its vapour is 8·716 compared with air, and 127 compared with hydrogen.

It is only soluble in water to the extent of 1 in 7000. It is more soluble in alcohol, and still more in ether, chloroform, benzene, and carbon disulphide, communicating a magnificent violet colour to these four last-named fluids. Its best ordinary solvent, as adopted in pharmacy, is a strong solution of potassium iodide ; 30 grains of which, dissolved in an ounce of water, will take up 20 grains of iodine. Its vapour, like that of chlorine, is very irritating ; but if not in large quantities it may be inhaled without giving rise to any ill effects. The melting point of iodine is 236° F., and it volatilizes at 356° F. It colours the skin brown, or, if in small quantities, yellow ; but the stain may be instantly removed by ammonium hydrate. Iodine possesses an intimate relation to chlorine and bromine in all its compounds, but its affinities are much more feeble. Free chlorine or bromine can therefore liberate iodine from all its combinations with basylous radicals by substitution, thus :—

$$2KI + Cl_2 = 2KCl + I_2.$$
$$2KI + Br_2 = 2KBr + I_2.$$

The combinations of iodine with oxygen and similar electro-negative elements are, on the other hand, more stable than those of chlorine and bromine. It combines directly with metals to form iodides, and when heated in the presence of water it can dissolve gold. It also acts, in the presence of water, as an indirect oxidizer, but more feebly than either chlorine or bromine. As its solution is not liable to rapid decomposition in contact with air and light, it is sometimes used in analysis in preference to these elements.

(*For detection and impurities of free Iodine, see Author's* Analytical Chemistry, *pages* 52 *and* 86.)

METALLIC IODIDES.

HYDROGEN IODIDE (SYN. *Hydriodic Acid*). **Formula, HI. Molecular Weight, 128.**

Like hydrochloric acid, this is truly a gas, very soluble in water. It is produced in solution by adding an acid, such as sulphuric acid, to potassium iodide. It cannot, however, be isolated thus, as the sulphuric acid on heating decomposes it and sets free iodine.

Practically it is prepared in solution,—

1. By passing sulphuretted hydrogen through iodine suspended in water, and filtering from the deposited sulphur :—

$$2H_2S + 2I_2 = 4HI + S_2.$$

2. By the action of water upon phosphorous iodide :—

$$PI_3 + 3H_2O = 3HI + H_3PO_3,$$

yielding hydriodic and phosphorous acids. This is usually done by packing a tube (closed at one end and furnished with a cork and delivery tube) with alternate layers of iodine, powdered glass moistened with water, and phosphorus, the use of the glass being simply to moderate the action.

$$4KI + 5I_2 + P_2 + 8H_2O = 14HI + 2K_2HPO_4.$$

Strong solution of hydriodic acid distilled over at a temperature of 260° F. has a specific gravity of 1.7, and as it contains 57 per cent. real HI, has the formula ($2HI + 11H_2O$). Lately hydriodic and hydrobromic acids have been prepared sufficiently pure for pharmaceutical purposes by simply shaking up a strong solution of potassium iodide with the slightest possible excess of tartaric acid :—

$$KI + H_2C_4H_4O_6 = HI + KHC_4H_4O_6,$$

and filtering out the precipitate of cream of tartar which forms. *Iodides* are salts which have iodine for their acidulous radical, acting as a monad. In two of its combinations, at least, namely ICl_3 and $I(C_2H_3O_2)_3$, I acts as a triad; but as neither of these compounds is of pharmaceutical importance, its atomicity may be taken as monad. Alkaline iodides are soluble, but many of those of heavy metals are insoluble, and are characterized by very brilliant colours. Insoluble iodides, as a rule, give up their iodine when digested with potassium hydrate, forming potassium iodide.

(*For detection, separation, and estimation of Iodides, see Author's* **Analytical Chemistry**, *pages* 52, 53, 150, 176, *and* 177.)

AMMONIUM IODIDE. Formula, NH_4I. Molecular Weight, 145.

Seldom used in Pharmacy, it may be prepared by precipitating ferrous iodide with ammonium carbonate. It is very deliquescent, and crystallizes in cubes. Iodine must not be added to ammonium hydrate, for the reason already stated (*see* **Iodide of Nitrogen**). It becomes coloured by exposure to the air from the liberation of a little iodine; but it may be restored to its original whiteness by a trace of a reducing agent, such as sulphuretted hydrogen or sulphurous anhydride.

SODIUM IODIDE. Formula, NaI. Molecular Weight, 150.

Prepared like potassium iodide, using sodium instead of potassium hydrate. It is rarely used in Pharmacy, probably on account of its unsightly and deliquescent nature; but in many cases its action is superior to that of potassium iodide, and it is employed by some high authorities in preference to that salt, as it exerts a less depressing influence.

POTASSIUM IODIDE (SYN. *Potassii Iodidum*). **Formula, KI. Molecular Weight, 166.**

Prepared by dissolving iodine in heated solution of potassium hydrate, which forms potassium iodide and iodate :—

$$6KHO + 3I_2 = 5KI + KIO_3 + 3H_2O;$$

and then evaporating to dryness, heating the residue with charcoal in a crucible, which changes the iodate into iodide, with evolution of carbonic oxide :—

$$KIO_3 + C_3 = KI + 3CO.$$

Potassium iodide is commonly met with in colourless, generally opaque cubic crystals, readily soluble in water, and in a less degree in spirit. It usually has a feebly alkaline reaction, and should be soluble in six parts of rectified spirit by weight. It is commonly adulterated with chlorides, carbonates, or iodates. The explanation of the test for iodate with tartaric acid and starch paste will be found under **Potassium Iodate.**

Potassium iodide is fusible by heat, and at a very high temperature it volatilizes unchanged. It is decomposed with the liberation of iodine by the following among others:—

Chlorine water.	Nitrous Acid.
Bromine Water.	*Calx and Soda Chlorata.*
Nitric Acid.	Ammonium Nitrate.
Sulphuric Acid (concentrated).	Potassium Ferricyanide.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 86.)

CADMIUM IODIDE (SYN. *Cadmii Iodidum*). **Formula, CdI_2. Molecular Weight, 366.**

Prepared by digesting iodine with metallic cadmium in the presence of water:—

$$Cd + I_2 = CdI_2.$$

The B.P. describes it as follows:—

In flat micaceous crystals, white, of a pearly lustre, which melt when heated to about 600° F., forming an amber-coloured fluid. At a dull red heat, violet-coloured vapours are given off (iodine). It is anhydrous and permanent in the air, freely soluble in water and in rectified spirit. The solution reddens litmus paper.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 86.)

CUPROUS IODIDE. Formula, CuI. Molecular Weight, 190·5.

Produced as a dirty-white precipitate on mixing solution of potassium iodide with a solution of 1 part cupric sulphate and 2·5 parts of ferrous sulphate. Neither chlorides nor bromides are affected by this reagent. (*For the equation see* **Purification of Iodine.**)

Cuprous iodide may also be formed from iodine and finely-divided copper, by heating them together in such a manner that the iodine vapour may pass over the metal at a red heat. By the action of potassium or sodium hydrate or carbonate upon it, cuprous oxide of a red colour is formed.

MERCUROUS IODIDE (SYN. *Hydrargyri Iodidum Viride*). **Formula, Hg_2I_2 or HgI. Molecular Weight, 327.**

By rubbing together mercury and iodine in proper proportions, in the presence of spirit, and drying in the dark.

$$\underset{200}{Hg} + \underset{127}{I} = \underset{327.}{HgI}, \text{ or more correctly } Hg_2 + I_2 = Hg_2I_2$$

Thus prepared, it is a dark green powder, insoluble in water, which darkens in colour upon exposure to light.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 86.)

It is most essential that the slightest excess of iodine should be avoided, as that would form the much more active *mercuric iodide.* This impurity is tested for by shaking up with ether, in which the mercurous iodide is insoluble,

while the mercuric iodide is soluble. The pure mercurous iodide should not be so green as the B.P. preparation, but more yellowish. On heating, it splits up into mercury and mercuric iodide, thus :—

$$2Hg_2I_2 = 2HgI_2 + Hg_2.$$

The same decomposition is induced by simple exposure to light; and this causes the chief objection to what would be otherwise a very excellent preparation for medicinal purposes.

Mercurous iodide may also be produced by precipitating mercurous acetate with potassium iodide. The nitrate is apt to yield an impure product. Besides this and the mercuric iodide, two other iodides are stated to exist (Hg_2I_3 and HgI_4); but they do not appear to be unquestionably chemical compounds, and are of *no importance to pharmacists.*

MERCURIC IODIDE (SYN. *Hydrargyri Iodidum Rubrum*). **Formula, HgI_2. Molecular Weight, 454.**

Prepared by precipitating a solution of mercuric chloride with potassium iodide, carefully avoiding excess :—

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$
$$271 + 332 = 454 + (149).$$

The equation shows that, to produce a proper effect, the ingredients must be in the proportion of 10 of mercuric chloride to $12\frac{1}{4}$ of potassium iodide, any excess of either, but especially of the latter, causing the precipitate to redissolve. In practice, the solutions are mixed boiling hot, and after the whole has cooled, the precipitate is filtered out, washed with cold water, and dried at 212°. Thus prepared, it is a crystalline powder, of a vermilion colour, becoming yellow when heated over a lamp on a sheet of paper; almost insoluble in water; dissolves sparingly in alcohol, but freely in ether or mercuric chloride, or potassium iodide. It is not soluble in boiling water.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 87.)

The property above mentioned of its turning yellow by heat, is extremely interesting. This is what is called a *dimorphous* body, *i.e.*, it can crystallize in two forms. In the ordinary precipitated condition it is not crystalline; it is then said to be *amorphous* (α, without; μορφή, shape). When heated it becomes yellow, and forms rhombic plates; if it be then touched by a cold steel knife, it will again become red, but will now assume the diamond (octahedral) form.

When chlorine is passed through mercuric iodide suspended in water, iodic chloride (ICl_3) and mercuric chloride result, the solution possessing a yellow colour.

An alkaline solution of mercuric iodide in potassium iodide is used for the detection and estimation of minute quantities of ammonia. It is called **Nessler's** solution. With very minute traces of ammonia, an orange coloration is produced on adding **Nessler**; but if any decided quantity be present, a copious reddish precipitate is formed.

FERROUS IODIDE (SYNS. *Ferri Iodidum. Iodide of Iron*). **Formula, FeI_2. Molecular Weight, 310.**

Prepared by the direct combination of iron and iodine in the presence of water :—

$$Fe_2 + 2I_2 = 2FeI_2.$$

The B.P. directs the iodine, iron, and water to be put into a flask, and

The only one which is of interest to us is :—

HYDROGEN IODATE (SYN. *Iodic Acid*).

Produced by the action of strong nitric acid and other oxidants upon iodine, but more practically prepared by suspending iodine in water and passing chlorine until complete solution is effected.

$$6H_2O + 5Cl_2 + I_2 = 2HIO_3 + 10HCl.$$

The solution thus obtained is saturated with sodium carbonate, and the iodic acid is precipitated out with barium chloride. The resulting precipitate of barium iodate is then filtered out, and exactly decomposed with dilute sulphuric acid :—

$$Ba2IO_3 + H_2SO_4 = 2HIO_3 + BaSO_4.$$

The iodic acid crystallizes out upon evaporation, as a hard and brilliant crystalline mass; it forms a class of salts called *iodates*, corresponding to chlorates, and having IO_3 as their acidulous radical. They are decomposed into iodides and oxygen by heat, and are also reduced by sulphurous acid.

(*For detection and separation of Iodates, see Author's* **Analytical Chemistry**, *pages* 53 *and* 54.)

POTASSIUM IODATE. Formula, KIO_3. Molecular Weight, 214.

Prepared by fusing potassium iodide with an oxidant, or more simply by mixing potassium chlorate and potassium iodide together, and digesting in water at a gentle heat, with a few drops of nitric acid to start the reaction, which is one of simple displacement of chlorine by iodine :—

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$

It will be remembered that the general rule of the inability of iodine to displace chlorine only holds good when it is combined with electro-positive radicals, not with oxygenated or electro-negative radicals. After the action the solution is boiled to expel chlorine, and evaporated to dryness. When solution of potassium iodate is added to sulphurous acid, iodine is liberated; it therefore forms the B.P. test for that acid :—

$$5H_2SO_3 + 2KIO_3 = 2KHSO_4 + 3H_2SO_4 + H_2O + I_2.$$

When excess of tartaric acid is added to potassium iodate, iodic acid is set free; and when the same acid is added to potassium iodide, hydriodic acid is set free, and potassium hydro-tartrate formed. Thus :—

$$5KI + KIO_3 + 6H_2C_4H_4O_6 = 5HI + HIO_3 + 6KHC_4H_4O_6.$$

If these acids be thus liberated together, they immediately decompose, forming water and free iodine :—

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

If therefore starch paste and tartaric acid be added to pure potassium iodide, no coloration takes place, because only hydriodic acid is liberated; but if the sample contains potassium iodate, an immediate production of free iodine ensues, which turns the starch blue.

HYPO-IODOUS ACID. Formula, HIO; and

HYPO-IODITES.

It is supposed that when iodine dissolves in an alkali a *hypo-iodite* is formed, and an iodide, as in the case of chlorine in *calx chlorata;* and that on heating it is decomposed into 5 of iodide and 1 of iodate.

PERIODIC ACID. Formula, HIO_4; and

PERIODATES.

Are prepared by further oxidizing sodium iodate, by means of chlorine; or by heating barium iodate in the air.

The acid is obtained from the barium salt by double decomposition with dilute sulphuric acid.

They are of no pharmaceutical importance.

Potassium iodate and ferric salts (such as $Fe_2 3SO_4$) yield a precipitate of ferric oxy-iodate—$(Fe_2{}^{vi}O)^{iv}4IO_3 8H_2O$, which when heated leaves pure Fe_2O_3.

(*For detection of Periodates, see Author's* **Analytical Chemistry**, *page* 54.)

COMPOUNDS OF IODINE WITH CHLORINE.

IODINE MONO-CHLORIDE. Formula, ICl.

Is prepared by passing chlorine over iodine till the whole is *just liquefied*, or by distilling iodine with potassium chlorate :—

$$3KClO_3 + I_2 = ICl + KCl + KIO_3 + KClO_4 + O_2.$$

It is a reddish-brown oily liquid with a suffocating odour and soluble in alcohol and ether. By spontaneous decomposition it yields **iodine tetrachloride** and free iodine :—

$$4ICl = ICl_4 + I_3.$$

IODINE TRICHLORIDE. Formula, ICl_3.

By passing chlorine *in excess* over iodine at a gentle heat. It is in orange-yellow crystalline needles, melting when heated gently. In contact with excess of water it forms hydrochloric acid, iodic acid, and iodine.

$$5ICl_3 + 9H_2O = 15HCl + 3HIO_3 + I_2.$$

CHAPTER VI.

OXYGEN AND ITS COMPOUNDS WITH SIMPLE BASYLOUS RADICALS.

OXYGEN. Symbol, O. Atomic Weight, 16. Atomicity, Dyad. Density, *referred to Hydrogen*, **16. Density,** *referred to Air*, **1·106. Weight of 1 litre,** *at* 0° C., 760 *mm.*, **1·437** *grammes.* **16 grammes,** *at* 0° C., 760 *mm.*, **occupy 11·2 litres.**

The discovery of this element by our fellow-countryman, Dr. Priestley, in 1774, its almost simultaneous isolation in Sweden by Scheele, and its subsequent careful study by Lavoisier, served to raise the curtain of doubt which had previously hung over the true science of Chemistry. The dream of the alchymist was ended, and the reign of sound inductive reasoning began. Although by the modern system of chemical theories it has been deposed from the place which it occupied as the great typical element and basis of the dualistic formulæ, it yet must retain its pre-eminence as the most abundant and widely-spread element in nature. Oxygen is not only found in a state of combination with every other element except fluorine, but it also exists free in the immense atmosphere by which the earth is surrounded, to the extent of one-fifth of its bulk. It is the active agent in combustion, and it is by means of oxygen that organized beings breathe, and are enabled to throw off the waste carbon from their tissues.

In a word, when we consider that the solid crust of the globe contains about one-half, and all the water on its surface eight-ninths of its weight of oxygen, the importance of the element cannot well be overrated.

Oxygen is prepared,—

1. **By heating some metallic oxides and peroxides**; for example.

(*a*) **Mercuric oxide**, heated, forms oxygen, which passes off, and Mercury, which sublimes and collects on the cool part of the apparatus :—

$$2HgO = Hg_2 + O_2.$$

(*b*) **Manganese peroxide**, heated to bright redness, yields oxygen and leaves manganoso-manganic oxide :—

$$3MnO_2 = Mn_3O_4 + O_2.$$

(*c*) **Red lead**, heated, gives off oxygen and leaves litharge (*plumbic oxide*) :—

$$2Pb_3O_4 = 6PbO + O_2.$$

(*d*) **Barium peroxide**, heated, yields oxygen and leaves barium oxide :—

$$2BaO_2 = 2BaO + O_2.$$

By again heating the BaO in contact with the air for some hours, the BaO_2 is reproduced, and thus a continuous process is obtained. The same remark also applies to the mercuric oxide and red lead processes.

2. **By heating salts rich in oxygen**, for example :—

(*a*) Potassium chlorate heated evolves oxygen and leaves potassium chloride :—

$$2KClO_3 = 2KCl + 3O_2.$$

The action really takes place in two stages, as already mentioned. (*See* **Potassium Chlorate,** *page* 66.)

(*b*) Potassium permanganate, heated, and superheated steam passed over it, forms oxygen and leaves a mixture of potassium hydrate and manganic oxide :—

$$K_2Mn_2O_8 + H_2O = 2KHO + Mn_2O_3 + 2O_2.$$

By passing a current of air over the residue while heated to dull redness, the original permanganate is re-formed. (*This is Tessie du Mothay's continuous process.*)

3. **By heating highly oxidized compounds with sulphuric acid,** for example :—

(*a*) Manganese peroxide, heated with sulphuric acid, forms manganous sulphate and oxygen :—

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

(*b*) **Potassium dichromate,** heated with sulphuric acid, forms potassium and chromic sulphates and gives off oxygen :—

$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_23SO_4 + 8H_2O + 3O_2.$$

(*c*) Potassium permanganate, heated with sulphuric acid, forms potassium and manganous sulphates, and evolves oxygen :—

$$2K_2Mn_2O_8 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 6H_2O + 5O_2.$$

(*d*) **Plumbic peroxide,** heated with sulphuric acid, forms plumbic sulphate and gives off oxygen :—

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2.$$

In addition to these general methods, oxygen can also be produced by several other special means, such as :—

(*a*) *The electrolysis of water,* during which oxygen is evolved at the positive electrode (or pole).

(*b*) By dropping sulphuric acid into a red-hot platinum retort, when it decomposes into sulphurous anhydride and oxygen, and the former may be removed by passing the mixed gases over lime or through an alkaline solution :—

$$2H_2SO_4 = 2SO_2 + 2H_2O + O_2.$$

(*c*) By passing chlorine and steam through a red-hot tube :—

$$2Cl_2 + 2H_2O = 4HCl + O_2.$$

The HCl may be removed by passing the gases into a cooled vessel containing water.

(*d*) By the action of the leaves of plants under the influence of direct sunlight, which decompose the carbonic anhydride of the air, assimilating the carbon and rejecting the oxygen.

Oxygen is a colourless, inodorous, and tasteless gas, which may be liquefied by a pressure of 500 atmospheres in a tube surrounded by solid carbonic anhydride giving a temperature of $-220°$ Fahr. On attaining this pressure the gauge suddenly falls to 320 atmospheres and remains stationary at that point; and when, by opening a stop-cock, the pressure is suddenly released, the oxygen appears as a jet of liquid. It is very slightly soluble in water, one hundred volumes of which are only capable of dissolving two and a half to

three volumes of the gas. All combustible bodies burn with greatly increased brilliancy when plunged into oxygen, and this fact may be splendidly illustrated by burning a piece of phosphorus under a bell jar filled with the gas. The hottest known flame is produced by causing hydrogen and oxygen to mix in the proportions necessary to form water, and burning the mixed gases at a suitable jet. This arrangement is known as the *oxyhydrogen blowpipe*. It is capable of melting platinum, and when urged upon a cylinder of quicklime it produces the very intense effect know as the *lime-light*. Many metals, notably iron and antimony, when introduced in the state of powder into a jar of oxygen, burn with brilliant scintillations.

The best practical method of preparing oxygen is to pound some potassium chlorate and dry it carefully at 212°. Then dry some powdered manganic peroxide carefully seeking for and removing any fragments of wood or other organic matter, which are often found accidentally mixed with the peroxide. The dry powders are then mixed by hand in the proportion of ¾ of the chlorate and ¼ of the peroxide and the mixture is placed in a small sheet iron retort connected with a washing bottle containing dilute solution of sodium hydrate. Heat is then gradually and cautiously applied, withdrawing the gas lamp if the evolution becomes too violent. The manganic peroxide is not decomposed, but only acts by catalysis to aid the oxygen to come off at a lower temperature and more regularly than when pure chlorate is used. (See Chap. II. page 10.)

OZONE. Symbol, O_3.

This particular modification of oxygen was discovered by Schonbein, and derives its name from the peculiar smell which it emits (ὄζω, to smell). It is produced whenever a series of electric discharges takes place in the air. Some authorities consider that ordinary free oxygen, which is comparatively inactive, results from the union of two active modifications, **ozone** and **antozone.** The nascent oxygen which is produced when permanganates or dichromates act as oxidizers, is viewed as being ozonic in its nature, while the extra atom of oxygen in peroxides, such as hydric, plumbic, and baric, is considered to be antozonic. This theory receives countenance from the fact that free oxygen may be produced from a mixture of potassium permanganate and hydric peroxide.

Ozone acts most violently as an oxidizer, and its presence in the air is ascertained by its power of liberating iodine from potassium iodide, and turning to a brown colour slips of white paper prepared with a solution of that salt.

The amount is estimated by the depth of colour. The slips are exposed in a box perforated with holes to admit air, and placed on the roof of an observatory or other building where the process is carried on. When there are grounds for suspecting that the air may contain traces of nitric or nitrous acid, which would also liberate iodine, turmeric or red litmus paper prepared with potassium iodide is substituted. The potassium hydrate produced by the action of moisture and ozone upon the iodide, turns the turmeric brown or the litmus blue. The presence of acid in the air lessens the delicacy of the test by neutralizing the liberated alkali, but cannot lead us to believe that ozone is present when it is really not.

For the purpose of comparison, a piece of neutral litmus paper must be exposed by the side of that moistened with potassium iodide, to indicate the error due to ammonia gas.

HYDRATES AND OXIDES.

Oxygen combines both with metalloids and metals. With the former it produces oxides, usually strongly electro-negative in their properties; while with the latter, its compounds exhibit as a rule equally well-marked electro-positive tendencies. Some of the oxides of metalloids are neutral; but the great bulk of them are capable of becoming true acids by uniting with the elements of water. They are called **anhydrides**, because they are viewed as being acids *minus* water, and were formerly known as *anhydrous acids*. The compounds of oxygen with metals or compound basylous radicals, are called simply **oxides** and they also possess the power of taking up the elements of water, forming **hydrates**. Like the anhydrides of metalloids, the oxides of the metals may be viewed as the hydrates minus water. A glance at the following equations will show this relationship:—

Cl_2O	+	H_2O	=	$2HClO$
Hypochlorous Anhydride.				Hypochlorous Acid
K_2O	+	H_2O	=	$2KHO$
Potassium Oxide.				Potassium Hydrate
$(SO_2)O$	+	H_2O	=	H_2SO_4
Sulphuric Anhydride.				Sulphuric Acid.
CaO	+	H_2O	=	$Ca2HO$
Calcium Oxide.				Calcium Hydrate.

The **acids** and the **hydrates** thus produced from their respective anhydrides or oxides, being in opposite states of electrical force, neutralize each other, and form salts with the elimination of water:—

$$2KHO + 2HClO = 2KClO + 2H_2O.$$
$$Ca2HO + H_2SO_4 = CaSO_4 + 2H_2O.$$

The anhydrides, together with their corresponding acids and the salts they produce, being treated of under their respective metalloids, it only remains for us to consider at this point the hydrates and oxides of simple basylous radicals (metals). These compounds may be classified as follows:—

1. **Hydrates**, are salts derived from water by the displacement of one atom of hydrogen by a basylous radical. They have hydroxyl (HO) for their acidulous radical, acting as a monad. The hydrates of the alkalies are freely soluble in water; those of calcium, magnesium, strontium, and barium are slightly so; but all other metallic hydrates are insoluble. Soluble hydrates are all strongly alkaline.

2. **Simple Oxides**, which are compounds of the metal and oxygen in proper proportion, according to their mutual atomicity, such as K_2O, CaO, PbO, or CuO. They are strongly basic in character, and possess the power of neutralizing acids to form salts with the elimination of water:—

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

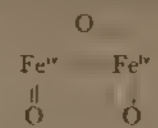
3. **Peroxides**, in which an atom of oxygen exists in excess of the amount found in the simple oxide. This extra atom of oxygen is very loosely combined, and the peroxides cannot form salts until it is removed. They are usually considered as being derived from hydric peroxide as the commencement of the series. Thus:—

H_2O_2	Hydric Peroxide.
BaO_2	Baric Peroxide.
MnO_2	Manganic Peroxide.
PbO_2	Plumbic Peroxide.

Their constitution is graphically represented as follows :—

Hydric Peroxide. Baric Peroxide.

4. **Sesquioxides.** These are compounds intermediate between oxides and peroxides, in which the oxygen is united with two atoms of a metal which are so self-saturated in their atomicity as to form together a hexad radical. Iron, which is truly a tetrad, may combine with another atom of itself to produce the hexad radical Fe_2, of which the oxide would be Fe_2O_3 thus :—



The metals capable of behaving in this way are iron, aluminium, chromium, and manganese ; and the oxides so produced are feeble bases, their salts being readily decomposed.

Oxides are detected by their negative characters. All those with which a pharmacist commonly meets are insoluble in water, except calcium, barium, and strontium oxides. They are all soluble in dilute nitric acid without odour or effervescence, and on the removal of their metal by either sulphuretted hydrogen, ammonium sulphide, or ammonium carbonate, a filtrate is obtained, which on evaporation to dryness and subsequent heating leaves no fixed residue.

HYDROGEN OXIDE (Syn. *Water*). **Formula, H_2O. Molecular Weight, 18.**

This all important body is known in three states :—

(1) In the gaseous form, as **steam** ; (2) In the fluid state, as **water** ; (3) In the solid condition, as **ice**. Water contracts by cold and expands by heat, but its contraction ceases at 39·2° F. (4° C.), and when cooled below that temperature it expands. Thus it follows that water is heaviest at 39·2° F. ; and it is by this beautiful provision of nature, that during frost the whole water in the world is prevented from flying into a solid mass of ice. Let us suppose that we have a lake with the air above it at a sharp frost. The water on the surface is cooled, and getting heavier it sinks ; and this action goes on until the whole body of water is nearly brought to 39·2° F. When the surface is cooled below that temperature, the surface water ceases to sink, and is converted into a sheet of ice, while the water below remains comparatively warm and protected. Water is converted into ice at 32° F. (0° C.), and it boils (forming steam) at 212° F. (100° C.) under ordinary conditions. On the removal of the pressure of the air, it boils at a much lower temperature ; and if, on the other hand, an increased pressure be exercised, the boiling point rises in proportion. Scientifically, the boiling point should be thus defined : *Water boils when the tension of its vapour equals the pressure of the superincumbent atmosphere.*

(*Other physical points respecting boiling and freezing are treated of in the Author's* **Analytical Chemistry**, *pages 5, 6, and 7.*)

The composition of water can be proved :—

1. By **Analysis.** When **steam** is passed over **red-hot iron**, ferroso-ferric oxide and hydrogen are formed :—

$$3Fe_2 + 8H_2O = 2Fe_3O_4 + 8H_2.$$

2. By **Synthesis.** When **two parts by volume of hydrogen** and **one part of oxygen** are mixed together, and a light applied, an amount of water is produced, which, if retained in the state of steam, would occupy two parts by volume:—

$$\begin{array}{ccccc} 2H_2 & + & O_2 & = & 2H_2O. \\ 4 \text{ vols.} & + & 2 \text{ vols.} & = & 4 \text{ vols.} \end{array}$$

3. By **Electrolysis.** On submerging the wires of a galvanic battery tipped with platinum plates in water, hydrogen gas is evolved at the negative pole (or tip wire from the zinc plate), and oxygen at the positive pole.

(*See Author's* **Analytical Chemistry,** *pages* 22 *and* 23.)

If these gases be collected, the hydrogen produced will be found to occupy *twice* the volume of the oxygen. If both quantities of gas be weighed, they will be found to be in the relation of 1 and 8 (= 2 and 16); and thus the formula of water is proved to be H_2O.

Water being the most universal solvent known, it therefore follows that all ordinary water holds impurities in solution. Natural waters may be classed as follows:—

1. **Rain water,** the purest form, which as a rule, however, contains traces of chlorides, ammonia, nitrates, etc.
2. **Spring** and **well waters,** which are waters rising from the earth, and consequently containing a large proportion of carbonates, chlorides, sulphates, and other salts, dissolved from the strata through which the water has passed.
3. **River water,** which is a mixture of spring and rain water, usually containing less mineral constituents than the last-described variety; but almost invariably contaminated with organic matter derived from various sources.
4. **Sea water,** which is loaded with sodium, magnesium, and other chlorides, and is called *salt water.*

The only way to obtain chemically pure water is by distillation. This is the *aqua distillata,* B.P.

HYDRIC PEROXIDE (SYNS. *Free Hydroxyl. Oxygenated Water*). **Formula, H_2O_2. Molecular Weight, 34.**

Is prepared by the action of **hydrochloric acid** on **barium peroxide**:—

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2.$$

The barium is removed by careful precipitation with dilute sulphuric acid (as barium sulphate), and the chlorine by a similar careful precipitation with argentic sulphate (as argentic chloride), and the excess of the sulphuric acid having been neutralized by barium carbonate, the whole is filtered, and the dilute solution of hydric peroxide thus obtained is concentrated by evaporation over sulphuric acid under the air-pump. A more simple process is to pass carbonic anhydride through barium peroxide suspended in water, thus:—

$$BaO_2 + CO_2 + H_2O = H_2O_2 + BaCO_3.$$

The majority of the metals form compounds analogous to hydroxyl, the most important of which are antimonyl, SbO (which exists in *tartar-emetic*), and bismuthyl, BiO (which forms the radical of *bismuthi subnitras,* B.P.). Hydric peroxide is a clear liquid, which neither freezes nor evaporates so readily as water. It is miscible with ether in certain proportions; the *ozonized ether,* as usually sold, being a solution in ether of a strength of 10 per cent. It is a powerful bleacher and disinfectant, and is also an active oxidizer. Some investigators have put forward the theory that the oxygen contained in hydric peroxide is in an antagonistic condition to that existing in the super-oxygen-

ated derivatives of chromium and manganese, and thus that oxygen has three modifications. These, they suppose, are, 1st, the *ordinary* or comparatively inactive; 2nd, the *negative* (in the permanganates, etc.); and 3rd, the *positive* (in hydric peroxide, baric peroxide, etc.) One of the bases upon which the idea depends is, that on adding a solution of hydric peroxide to chromates, manganates, or permanganates, in solution, an abundant evolution of oxygen takes place. This is explained by supposing that the negative or ozonic oxygen neutralizes the positive or antozonic. On this theory chromates, manganates, or permanganates, are termed *ozonides*.

LITHIUM HYDRATE (Syn. *Lithium Hydroxide*). **Formula, LiHO. Molecular Weight, 24.**

Is best prepared by the action of **barium hydrate** upon **lithium sulphate**, thus:—

$$Li_2SO_4 + Ba2HO = 2LiHO + BaSO_4.$$

The lithium hydrate remains in solution, and crystallizes out upon evaporation. It is much less soluble than potassium hydrate.

LITHIUM OXIDE (Syn. *Lithia*). **Formula, Li_2O. Molecular Weight, 30.**

When lithium hydrate is heated strongly, water is driven off, and this oxide remains:—

$$2LiHO = Li_2O + H_2O.$$

It is a white alkaline substance, communicating a scarlet or rose-coloured tint to the flame of a Bunsen burner.

AMMONIUM HYDRATE (Syns. *Liquor Ammoniæ Fortior. Spirit of Hartshorn. Spiritus Volatilis Cornu Cervi. Ammonium Hydroxide*). **Formula, NH_4HO. Molecular Weight, 35.**

Is generally called the *volatile alkali*. It is prepared by generating ammonia gas from **ammonium chloride** by **calcium hydrate**:—

$$2NH_4Cl + Ca2HO = 2NH_3 + CaCl_2 + 2H_2O,$$

and then passing this gas into water:—

$$2NH_3 + 2H_2O = 2NH_4HO.$$

The ammonia gas (NH_3) not only displaces the hydrogen of the water, but combines with the atom of hydrogen so displaced, and forms the metallic radical **ammonium** (NH_4), which unites with the hydroxyl radical to form a hydrate (NH_4HO). (*See* **Ammonia**.)

In practice the gas is generated in an iron bottle placed in a sand bath and connected first with two empty Woulff's bottles and then with a matrass containing water, and heat is applied till gas ceases to pass. During the process a coloured and impure liquid collects in the two empty bottles, and by distilling this into water a further quantity of pure *liquor* is obtained.

Thus made, *liquor ammoniæ fortior* is a colourless liquid with a characteristic and very pungent odour, and a strongly alkaline reaction. Specific gravity, 0·891. One fluid drachm contains 15·83 grains of ammonia (NH_3), or 32·5 per cent. When heated for a time and the loss of water made up, all the ammonia passes off and leaves pure water. This also occurs slowly by exposure to the air.

The *liquor ammoniæ*, B.P., is made by adding two volumes of water to one volume of the stronger solution. It has a specific gravity of ·959, though

the B.P. says ·959. Each hundred measures of a mixture composed of two measures of water and one of *liquor ammoniæ fortior*, after mixture, expands half a measure. That is, if we mix one volume of the solution having ·891 specific gravity, and two volumes of water, the specific gravity of the mixture will be ·957 instead of ·964 as it would be if no expansion took place.

(*For analysis, impurities, and estimation of Liquor Ammoniæ, see Author's* **Analytical Chemistry**, *pages* 88 *and* 154.)

SODIUM HYDRATE (SYNS. *Soda Caustica, B.P. Soda. Sodium Hydroxide. Hydrated Soda*). **Formula, NaHO. Molecular Weight, 40.**

Is first prepared in the form of *liquor sodæ* by boiling solution of sodium carbonate and calcium hydrate, and then that liquid evaporated yields solid NaHO, called *soda caustica* :—

$$Na_2CO_3 + Ca2HO = 2NaHO + CaCO_3.$$

In practice 28 ounces of sodium carbonate are heated with a gallon of distilled water in a clean iron pot, and when it boils 12 ounces of slaked lime are stirred in. Ebullition is continued for 10 minutes and the whole is closely covered, allowed to settle, and the clear liquor drawn off with a siphon. The solution thus obtained is colourless and strongly alkaline. It feels soapy between the fingers and neutralizes acids without effervescence. It has a specific gravity of 1·047 and contains 18·8 grains of NaHO in each fluid ounce.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 88.)

The solid sodium hydrate obtained by the evaporation of the liquid above described is in hard greyish-white masses, very alkaline and corrosive, and readily fusible by heat.

Sodium hydrate is less readily volatilized than potassium hydrate. Combined with 7 molecules of water it forms colourless, clear crystals. When an alkaline salt is required, the acidulous radical of which is alone valuable, the sodium compound is prepared, as, in consequence of its smaller atomic weight, a less amount of it will be required than of the corresponding potassium salt.

POTASSIUM HYDRATE (SYNS. *Potassa Caustica, B.P. Hydrated Oxide of Potash. Potassium Hydroxide*). **Formula, KHO. Molecular Weight, 56.**

Prepared in absolute purity by burning **potassium** on distilled **water**, and evaporating the solution in a silver dish :—

$$K_2 + 2H_2O = 2KHO + H_2.$$

According to the B.P., it is first prepared in solution, as *liquor potassæ* by boiling a solution of **potassium carbonate** with **calcium hydrate** :—

$$K_2CO_3 + Ca2HO = 2KHO + CaCO_3.$$

The process is exactly similar in detail to that already described for *liquor sodæ*.

Liquor potassæ is also similar in appearance and properties to *liquor sodæ* ; but its specific gravity is 1·058 and it contains 27 grains solid KHO per fluid ounce.

(*For analysis, impurities, and estimation, see Author's* **Analytical Chemistry**, *pages* 89 *and* 154.)

A purer liquor than that of the B.P. may be made by avoiding the use of heat and letting the ingredients react slowly in a stoppered bottle. It is worthy of note, that the solution of potassium carbonate should be no stronger than directed, seeing that with a very concentrated solution no

action would ensue; or, if it did, it would be at once reversed, and rendered abortive, because it has been found that calcium carbonate can be converted back to the hydrate by strong boiling potassium hydrate, thus

$$CaCO_3 + 2KHO = K_2CO_3 + Ca2HO.$$

From *liquor potassæ* the solid hydrate is prepared by simple evaporation.

It is called *potassa caustica*, and is in hard white lumps or pencils, very deliquescent and powerfully alkaline and corrosive.

Potassium hydrate in solution possesses the power of dissolving aluminium oxide, and as that substance is present in the calcium hydrate used to manufacture the *liquor*, it follows that nearly all ordinary samples contain aluminium. This may be removed by dissolving in alcohol, in which potassium hydrate is soluble, while aluminium hydrate and potassium carbonates are insoluble.

Liquor Potassæ, when kept in ordinary flint glass bottles, attacks them slowly, and dissolves out silica and lead. The former makes it unfit for use in analysis, and the latter is dangerous, and may be detected by blackening with sulphuretted hydrogen. The bottles best adapted for holding solution of potassium hydrate are those which do not contain lead in their composition, being made of superior glass, or, failing them, ordinary green glass bottles. These same remarks apply to *liquor sodæ*.

SODIUM and POTASSIUM OXIDES.

The following are the series of oxides formed by these metals. They are difficult to isolate, and are not likely to be met with by the pharmacist, who deals only with the hydrates.

The protoxides are prepared by heating a molecular weight of the hydrate with an atomic weight of the metal.

$$2KHO + K_2 = 2K_2O + H_2.$$

Protoxides	Na_2O.	K_2O
Dioxides	Na_2O_2.	K_2O_2
Peroxides	None discovered.	K_2O_4

ARGENTIC OXIDE (SYN. *Argenti Oxidum, B.P.*). **Formula, Ag_2O. Molecular Weight, 232.**

Prepared by the action of **calcium hydrate** on **argentic nitrate**:—

$$2AgNO_3 + Ca2HO = Ag_2O + Ca2NO_3 + H_2O.$$

The argentic nitrate is to be dissolved in water and the solution having been poured into an excess of limewater, the precipitate is collected and dried at 212° F. and the resulting oxide preserved in a stoppered bottle.

Argentic oxide is an olive brown powder, which at a low red heat gives off oxygen, and is reduced to the metallic state. It is insoluble in water but dissolves completely in nitric acid, without the evolution of any gas, forming a solution which has the characters of argentic nitrate.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 90.)

When ammonium hydrate is added to argentic nitrate, the precipitated oxide redissolves in excess, and the solution thus produced is called *ammonio-nitrate of silver*, and used as a test for arsenious and arsenic acids. Argentic oxide, digested in strong liquid ammonia, is converted into an exceedingly dangerous compound, called *fulminating silver*. Argentic peroxide, Ag_2O_2, is also known; and an argentous oxide, Ag_4O, has been isolated.

CALCIUM HYDRATE (SYNS. *Slaked Lime. Calcis Hydras. Calcium Hydroxide*). **Formula, Ca2HO. Molecular Weight, 74.**

Prepared by the action of **water** upon **calcium oxide**, the action being called *slaking*:—

$$CaO + H_2O = Ca2HO.$$

The lime is placed in a metal pot, some water is poured upon it, and when vapour ceases to be disengaged, the pot is covered until cool. The slaked lime is then sifted on an iron-wire sieve, rejecting what does not pass through. The sifted powder should be kept in a stoppered bottle.

Calcium hydrate is powerfully alkaline, and when heated re-forms the oxide. It is not readily produced from calcium oxide which contains much silica and aluminium oxide; but in such a case the employment of hot water accelerates its formation.

Calcium hydrate is peculiar, inasmuch as it is more soluble in cold than in boiling water. Phillips, who has practically investigated this property, supplies the following table:—

One pint	of water at	30° F.	dissolves	$13\frac{1}{4}$	grains.
"	"	60°	"	$11\frac{6}{10}$	"
"	"	212°	"	$6\frac{7}{10}$	"

It is for this reason that the B.P. prepares its *liquor calcis* (limewater) with cold water, by placing 2 ounces of lime in a stoppered bottle and adding a gallon of water, shaking well, and letting the whole stand for 12 hours.

(*For analysis, impurities, and estimation, see Author's* **Analytical Chemistry**, *pages* 89 *and* 154.)

If kept carefully from the air, the same amount of calcium hydrate will bear four such treatments with water, and yield each time a full strength liquor. There are many substances, notably the alkalies, which almost entirely prevent the solution of calcium hydrate in water; whilst there are also many which largely increase its solubility. Among the latter may be mentioned sugar, mannite, and glycerin. Sugar acts by combining with the calcium hydrate to form calcium saccharate, and although thus combined the calcium hydrate still continues to exhibit all its alkaline properties. The solution is termed in the B.P. *liquor calcis saccharatus*, in which 1 ounce of Ca2HO is steeped in a pint of water containing 2 ounces of refined sugar and a solution produced having a specific gravity of 1·052.

When strong, this liquid becomes gelatinous on boiling, owing to separation of the lime salt, but it becomes clear again on cooling. Exposed to the air, it absorbs carbonic acid gas, and the calcium separates out as carbonate, as in the case of ordinary limewater. The precipitate is a compound in which the sugar acts as a hexad.

CALCIUM OXIDE (SYNS. *Calx, B.P. Lime*). **Formula, CaO. Molecular Weight, 56.**

Is prepared by heating native **calcium carbonate** (*chalk* or *limestone*) until **all the carbonic anhydride** is driven off:—

$$CaCO_3 = CaO + CO_2.$$

The operation is conducted in an arrangement called a *kiln*. This is a circular tower of brickwork or stone, the interior of which is made in the shape of a funnel. A furnace is constructed at one side, so that the heat enters the funnel a little way above the bottom.

The kiln having been filled with limestone, the heat of the furnace acts

upon it, and converts it into calcium oxide, which is drawn off at the bottom, while new mineral is constantly poured in at the top, and so the action goes on night and day. The product is commonly called *quicklime*. It is usually met with in compact masses of a whitish colour, which readily absorb water, and which, when rather less than their weight of water is added, crack and fall into powder, with the development of much heat.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 90.)

The powder obtained by the process of *slaking*, when agitated with distilled water, gives, after filtration, a clear solution which has an alkaline reaction. It is infusible by the heat of any furnace.

(For the remaining facts concerning calcium oxide, *see* **Calcium Hydrate.**)

Calcium also forms a *peroxide*, CaO_2, of little interest.

STRONTIUM HYDRATE (SYN. *Strontium Hydroxide*). **Formula, Sr2HO.**

Approximates to barium hydrate in all its properties. It may be made by a similar process. When prepared by slaking strontium oxide, it forms a crystalline mass. It is of no practical interest.

STRONTIUM OXIDE (SYN. *Strontia*). **Formula, SrO.**

A powder having very nearly the same qualities as barium oxide. It is prepared in the same manner as that body, but is very little used. It is soluble to the extent of 2 per cent in water at 60° F., and 4 per cent. at 212° F. In the other methods of formation it resembles barium oxide.

BARIUM HYDRATE (SYN. *Barium Hydroxide*). **Formula, Ba2HO. Molecular Weight, 171.**

Very much resembles calcium hydrate, and, like it, is slightly soluble in water, the solution being called *baryta water*. It is prepared by slaking barium oxide, and also by digesting barium sulphide with cupric oxide and water. It dissolves in water to the extent of 1 in 20 of cold and 1 in 2 of boiling, and can be procured in crystals having the formula $Ba2HO,4H_2O$. It is decidedly alkaline, and is used to separate magnesium from the alkaline metals by precipitating it as hydrate.

(*See estimation of Potassium in Author's* **Analytical Chemistry.**)

BARIUM OXIDE (SYN. *Baryta*). **Formula, BaO. Molecular Weight, 153.**

Is prepared by heating **baric nitrate** in a crucible to a bright red heat until decomposed; oxygen, nitrogen, and nitric peroxide being evolved:—

$$2Ba.2NO_3 = 2BaO + 2NO_2 + 3O_2 + N_2.$$

It is a whitish, earthy mass, easily pulverized, and combining with water to form **barium hydrate.**

BARIC PEROXIDE. Formula, BaO_2. Molecular Weight, 169.

Prepared by heating **barium oxide** to dull redness in contact with air or oxygen. The hydrate may be employed; but it is then necessary to mix it with magnesium oxide to prevent its fusion, as, when fused, oxygen would not be so readily absorbed:—

$$2BaO + O_2 = 2BaO_2.$$

When treated with **hydrochloric acid**, it yields **hydric peroxide** and **barium chloride** :—

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

MAGNESIUM HYDRATE (SYNS. *Hydrated Magnesia. Magnesium Hydroxide*). **Formula, Mg2HO. Molecular Weight, 58.**

A white precipitate produced in soluble salts of magnesium by either potassium or sodium hydrate, and also by barium hydrate :—

$$MgSO_4 + 2NaHO = Mg2HO + Na_2SO_4.$$

This precipitate is soluble in all ammoniacal salts, and most of all in ammonium chloride; and it therefore cannot be produced in the presence of that substance.

It is for this reason that ammonium chloride is added before ammonium sulphide, when precipitating metals of the third group, in qualitative analysis, the magnesium being thereby held in solution, to be afterwards precipitated by sodium phosphate. In perfectly neutral magnesium sulphate, a precipitate of magnesium hydrate is produced by *liquor ammoniæ*; but if the solution be slightly acid, such a precipitate is not formed, because the ammonium hydrate in neutralizing the acid produces an ammoniacal salt. Magnesium hydrate is not soluble in excess of its precipitants. It is very slightly soluble in water, and when heated forms the oxide.

MAGNESIUM OXIDE (SYNS. *Magnesia. Magnesia Levis, B.P.*). **Formula, MgO. Molecular Weight, 40.**

Is prepared by heating **magnesium carbonate** in a crucible until a portion taken from the centre ceases to effervesce with dilute sulphuric acid (thus showing that all the carbonic anhydride has been expelled). The B.P. carbonate is a mixture of magnesium carbonate, magnesium hydrate, and water. The reaction, therefore, is :—

$$(MgCO_3)_3Mg2HO4H_2O = 4MgO + 3CO_2 + 5H_2O.$$

When *magnesiæ carbonas* is thus treated it yields **magnesia**, while from *magnesiæ carbonas levis* **magnesia levis** is produced. These two oxides are alike in chemical constitution, and differ only in the degree of aggregation of their molecules, a fact demonstrated by the experiments of Mr. Deane; the *magnesia* being close and heavy, while the *magnesia levis* is light and porous. Both varieties are white powders, soluble in dilute acids without effervescence. They are practically insoluble in water, only dissolving sufficiently to show a slight alkaline reaction with delicate neutral litmus paper.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 90.)

Magnesium oxide may also be prepared by burning the metal magnesium in the air or in oxygen.

ZINC HYDRATE (SYNS. *Zinc Hydroxide. Hydrated Oxide of Zinc*). **Formula, Zn2HO. Molecular Weight, 99.**

A white precipitate produced by potassium, sodium, or ammonium hydrates, from solutions containing zinc. It is *immediately soluble in excess of the precipitants;* and the solution thus obtained, when treated with ammonium sulphide, deposits white zinc sulphide. By this means zinc may be separated from iron and aluminium.

ZINC OXIDE (SYNS. *Zinci Oxidum. Zinc White*). **Formula, ZnO. Molecular Weight, 81.**

Prepared (by Hubbock's process) by heating zinc in a crucible placed in the centre of a chamber with free access of air. When heated to whiteness the zinc takes fire, burning with a light blue flame, forming large flakes of the oxide, which collect on the floor of the chamber.* The oxide is freed from the particles of metallic zinc mechanically thrown out owing to the violence of the action, by mixing with water, stirring rapidly, and pouring off as soon as the heavy metallic particles have settled.

This process is called *levigation.*

The action during the burning of the zinc is one of direct combination with the oxygen of the air:—

$$2Zn + O_2 = 2ZnO.$$

The oxide thus produced is perfectly white, while the B.P. oxide is yellowish white. By the B.P. process zinc oxide is prepared by heating the official carbonate in a crucible until a portion taken from the centre ceases to effervesce with diluted sulphuric acid.

As in the case of magnesia, the official zinc carbonate is a mixture of carbonate, hydrate, and water, and on heating a similar action takes place to that already described under *magnesia*.—

$$ZnCO_3(Zn2HO)_2H_2O = 3ZnO + CO_2 + 3H_2O.$$

Thus made, zinc oxide is a soft nearly white powder, tasteless and inodorous, becoming pale yellow when heated, but resuming its original colour on cooling. It is insoluble in water, but dissolves without effervescence in dilute acids.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 91.)

Zinc is usually estimated in this form.

CUPRIC HYDRATE (SYNS. *Cupric Hydroxide. Hydrated Oxide of Copper*). **Formula, Cu2HO. Molecular Weight, 97·5.**

A bluish precipitate, rapidly turning black, owing to the formation of cupric oxide. It is produced in a soluble cupric salt by addition of potassium or sodium hydrates. The precipitate is insoluble in excess, but in the presence of organic matters, and notably of Rochelle salt, it immediately re-dissolves to form a blue liquid, which on being boiled with sugar deposits *cuprous oxide.* This solution is called *Fehling's solution for the estimation of sugar.*

(*See Author's* **Analytical Chemistry**, *page* 159.)

When ammonium hydrate is added to cupric sulphate, it produces a precipitate of hydrate, which, however, instantly re-dissolves in excess, forming a deep blue solution, due to the production of *cupric tetrammonium sulphate* ($CuSO_4 4NH_3.H_2O$). (*See* **Sulphates.**)

The liquid thus obtained is commonly called ammonio-sulphate of copper, and is used as a reagent for the detection of arsenious acid, with which it forms a precipitate of *Scheele's green* (cupric arsenite).

CUPROUS OXIDE (SYN. *Suboxide of Copper*). **Formula, Cu_2O. Molecular Weight, 143.**

Is a brick-red substance, produced when copper is heated in an imperfect

* Zinc oxide prepared by this method was formerly known as "philosophical wool," and as "flowers of zinc."

supply of air. It is also precipitated by boiling grape sugar with a solution of copper in the presence of excess of an alkaline hydrate. This is the foundation of Strommer's and Fehling's tests for sugar.

CUPRIC OXIDE (SYN. *Black Copper*). **Formula, CuO. Molecular Weight, 79·5.**

A brownish black substance, formed in scales on the surface of copper heated in contact with the air, and also in powder by heating **cupric nitrate.** It is much used for the ultimate analysis of the carbonaceous (organic) bodies, which it converts, at a red heat, into carbonic anhydride and water, becoming itself reduced to cuprous oxide.

(*For details of this process, see Author's* **Analytical Chemistry**, *page* 181.)

It is remarkable for its hygroscopic nature, that is to say, the eagerness with which it absorbs moisture from the air. It should therefore be kept in closely stopped bottles, and always be re-ignited before use.

Copper is frequently estimated in this form.

(*See Author's* **Analytical Chemistry**, *page* 167.)

CUPRIC PEROXIDE. Formula, CuO_2.

Is also known (CuO_2); but the existence of a sesquioxide (Cu_2O_3) is only inferred, not having been yet definitely isolated.

MERCUROUS OXIDE (SYN. *Suboxide of Mercury*). **Formula, Hg_2O. Molecular Weight, 416.**

Prepared by treating a **mercurous salt** with any **alkaline hydrate**, except ammonium hydrate. It is the active ingredient in *lotio hydrargyri nigra*, B.P., which is prepared by the action of limewater (**calcium hydrate**) upon calomel (**mercurous chloride**):—

$$Hg_2Cl_2 + Ca2HO = Hg_2O + CaCl_2 + H_2O.$$

The lotion thus prepared usually contains unaltered calomel, and is not by any means a reliable mixture, because by exposure to light it forms metallic mercury and mercuric oxide. This change is detected by testing the clear portion poured off from the sediment with calcium or potassium hydrate, when it will turn yellow if mercuric oxide has been formed and dissolved.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 91.)

Mercurous oxide is a black powder insoluble in water and also in hydrochloric acid (distinction from mercuric oxide). Heated, it forms mercuric oxide and metallic mercury.

MERCURIC OXIDE (SYNS. *Hydrargyri Oxidum Flavum. Hydrargyri Oxidum Rubrum*). **Formula, HgO. Molecular Weight, 216.**

Prepared (1) by prolonged heating of mercury in contact with the air:—

$$Hg_2 + O_2 = 2HgO.$$

The product is dark-red in colour and *distinctly crystalline.*

(2) By precipitation of a **mercuric salt** with any **alkaline hydrate** except ammonium hydrate.

The B.P. prepares it in *lotio hydrargyri flava* by precipitating solution of **mercuric chloride with limewater (calcium hydrate)**:—

$$HgCl_2 + Ca2HO = HgO + CaCl_2 + H_2O.$$

(3) In the form of *hydrargyri oxidum flavum*, B.P., it is prepared by precipitating a solution of **mercuric chloride** with **sodium hydrate** and drying the precipitate in a water bath :—

$$HgCl_2 + 2NaHO = HgO + 2NaCl + H_2O.$$

Thus produced, it is an *amorphous* yellow powder, practically insoluble in water, but readily soluble with effervescence in diluted hydrochloric acid. Although, as already stated, it is practically insoluble, yet it communicates to water an alkaline reaction to delicate litmus paper, and a metallic taste.

(4) As *hydrargyri oxidum rubrum*, B.P., it is prepared by mixing **mercuric nitrate** with **metallic mercury**, and heating until no more red fumes of nitric peroxide are given off :

$$2Hg2NO_3 + Hg_2 = 4HgO + 2N_2O_4$$

In this form it is an orange-red powder, readily dissolved by hydrochloric acid, and *very crystalline* in structure. It is entirely volatilized by heat under redness, being at the same time decomposed into mercury and oxygen.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 91.)

Mercuric oxide is reduced to mercurous oxide, or even to the metallic state, when mixed with readily oxidizable substances, such as the first product of the oxidation of fats or nitrogenous bodies. The common adulterations are (1) *Red lead*, which is detected by the formation of a precipitate of plumbic peroxide when the sample is dissolved in dilute nitric acid. (2) *Undecomposed basic mercuric nitrate*, detected by red fumes on heating. (3) *Brick dust*, remains insoluble in dilute nitric acid, and is known by its appearance. (4) *Cinnabar* (native red mercuric sulphide) is left as a residue on dissolving the sample in dilute hydrochloric acid. (5) *Mercurous oxide*, is also insoluble in hydrochloric acid, as well as calomel, which is sometimes, but rarely found.

ALUMINIUM HYDRATE (SYNS. *Aluminic Hydroxide, Hydrated Oxide of Aluminium, Hydrated Alumina.*) **Formula, $Al_2 6HO$. Molecular Weight, 157.**

Is the precipitate produced in alum, or any soluble salt of aluminium, by ammonium hydrate, carbonate, or sulphydrate. When produced it is not absolutely insoluble, but can be rendered so by boiling off the excess of volatile ammonium salts. It is precipitable by potassium or sodium hydrates, but is readily soluble in excess of either, separating out if the alkaline solution be boiled with ammonium chloride. When heated to redness it is converted into aluminium oxide.

Aluminium hydrate is often employed in dyeing, as a *mordant* to fix various colouring matters in the texture of wool, silk, or cotton. It is usually formed on the fibres of the fabrics by first steeping them in "alum" or aluminium acetate, and then passing through a solution of an alkaline carbonate or hydrate.

ALUMINIUM OXIDE (SYNS. *Alumina, Sesquioxide of Aluminium*) **Formula, Al_2O_3. Molecular Weight, 103.**

A horny looking, white mass, obtained by heating aluminium hydrate to redness :—

$$Al_2 6HO = Al_2O_3 + 3H_2O.$$

After ignition it is only soluble in the strongest boiling hydrochloric acid. *Aqua regia* dissolves it ; and fusion with acid potassium sulphate causes it to

dissolve readily in dilute hydrochloric acid. It is in this form that aluminium is usually estimated.

(*See Author's* **Analytical Chemistry**, *page* 172.)

MANGANOUS HYDRATE (SYN. *Manganous Hydroxide*). **Formula, Mn2HO.**

Is formed on the addition of an alkaline hydrate to manganous salts as white precipitate: soluble in excess of ammonium hydrate in the presence of ammonium chloride, but insoluble in potassium and sodium hydrates:—

$$MnCl_2 + 2KHO = Mn2HO + 2KCl.$$

It is speedily converted into Mn_3O_4 or Mn_2O_3 by exposure to the air.

MANGANESE OXIDES.

Manganese forms a long series of oxides, as follows:—

Manganous Oxide	MnO.
Manganoso-manganic Oxide	Mn_3O_4.
Manganic Oxide	Mn_2O_3.
Manganic Peroxide	MnO_2.
Permanganic Anhydride	Mn_2O_7.

MANGANOUS OXIDE. Formula, MnO.

A light green body formed by heating manganous oxalate out of contact with the air, which is not of pharmaceutical importance.

MANGANOSO-MANGANIC OXIDE. Formula, Mn_3O_4.

Prepared by heating the peroxide to redness, when it gives up oxygen, and leaves this oxide as a red residue. (*See* **Oxygen.**)

Manganese is best estimated in this form.

MANGANIC OXIDE. Formula, Mn_2O_3.

Found native in *Braunite.* It is brown in colour, and of no interest to the pharmacist.

MANGANIC PEROXIDE (SYNS. *Black Oxide of Manganese. Pyrolusite*). **Formula, MnO_2. Molecular Weight, 87.**

Is the chief source of manganese, extensively used in the arts for many purposes, notably the manufacture of chlorine. In its native state it is called *pyrolusite*, owing to the extreme readiness with which its composition is loosed or resolved by heat (*πῦρ, λύσις*).

(*For analysis, see Author's* **Analytical Chemistry**, *page* 91.)

It is an oxidizer, either when treated alone or with sulphuric acid. (*See* **Oxygen.**) It dissolves in hydrochloric acid, yielding manganous chloride, and evolving chlorine gas. When this gas is passed through a solution of manganous salt (in the presence of an alkali), the following reaction occurs:—

$$MnCl_2 + Cl_2 + 2H_2O = MnO_2 + 4HCl.$$

When treated with oxalic acid and sulphuric acid, it dissolves, forming manganous sulphate, converting the oxalic acid entirely into carbonic anhydride and water:—

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = MnSO_4 + 2CO_2 + H_2O.$$

This reaction is taken advantage of to estimate the value of samples of the ore.

MANGANIC ANHYDRIDE. Formula, MnO_3.

Is itself unknown, but is presumed to exist, and to combine with water to form manganic acid :—

$$MnO_3 + H_2O = H_2MnO_4.$$

For although we cannot isolate even the latter body, we have a class of salts called **manganates**, which have MnO_4 for their acidulous radical, acting as a dyad.

POTASSIUM MANGANATE. Formula, K_2MnO_4.

Is a green soluble substance, produced by calcining **manganic peroxide** with **potassium hydrate**, in contact with the air. Frequently a little potassium chlorate is added to hasten the oxidation.

SODIUM MANGANATE,

Which is made in the same way, using sodium hydrate, is the basis of Condy's green disinfecting fluid.

Manganates are powerful oxidizers, and are decolorized by oxalic acid, or any reducing agent, as well as by sulphuretted hydrogen and putrid organic matters.

Dissolved in a quantity of hot water, they form permanganate, and deposit manganic peroxide.

PERMANGANIC ANHYDRIDE. Formula, Mn_2O_7.

Can be isolated by the action of strong sulphuric acid upon potassium permanganate, in the presence of a freezing mixture. It unites with water to form solution of permanganic acid, $H_2Mn_2O_8$, a deep violet liquid, very unstable, and explosive when exposed to sudden sunlight.

POTASSIUM PERMANGANATE (SYN. *Potassæ Permanganas*). **Formula, $K_2Mn_2O_8$ = $2KMNO_4$. Molecular Weight, 316.**

Is prepared by fusing **potassium hydrate** with **manganic peroxide** and a little **potassium chlorate**, forming **potassium manganate** :

$$6KHO + 3MnO_2 + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O.$$

On boiling the green mass in water, it forms a purple solution containing **potassium permanganate** and potassium hydrate, manganic peroxide being deposited :—

$$3K_2MnO_4 + 2H_2O = K_2Mn_2O_8 + MnO_2 + 4KHO.$$

Sulphuric acid is added in sufficient quantity to neutralize the potassium hydrate produced in this last reaction, and the whole crystallized.

As is prepared, it is found in dark purple, slender, prismatic crystals, inodorous, with a sweet astringent taste, soluble in water.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 92.)

Potassium permanganate is a powerful direct oxidizer, yielding up its oxygen very readily, and being itself decolorized. It is thus very useful for the estimation of readily oxidized substances.

For instance, in contact with oxalic acid, acidulated with sulphuric acid, it is instantly decomposed :—

$$K_2Mn_2O_8 + 3H_2SO_4 + 5H_2C_2O_4 = 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O.$$

Thus it is evident that one molecule of $K_2Mn_2O_8$, or two molecules of $KMnO_4$, require five molecules of oxalic acid for complete decolorization. The strength of a permanganate solution may therefore be obtained by acidulating a known quantity with sulphuric acid, and adding volumetric solution of oxalic acid until the liquid is just decolorized, and having ascertained the number of c.c. of oxalic acid used, calculate thus :—

$$\frac{(\text{c.c. oxalic acid used} \times \cdot 063) \times 316}{630} = \left\{\begin{array}{l}\text{amount of potassium permanganate in} \\ \text{weight of solution taken for analysis.}\end{array}\right.$$

Potassium permanganate also raises ferrous into ferric salts, in the presence of sulphuric acid, and is itself decolorized, as with oxalic acid :—

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = 5Fe_23SO_4 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

This equation shows that one molecule of potassium permanganate (316) can raise 10 molecules of iron (560) from the ferrous to the ferric state.

SODIUM PERMANGANATE. Formula, $Na_2Mn_2O_8$.

Prepared like the last-described salt, using sodium instead of potassium hydrate. It is the basis of *Condy's crimson fluid*, which disinfects by direct oxidation, and of *Chlorozone*, which is essentially a solution containing at once sodium permanganate and sodium hypochlorite, and therefore acts both by direct and indirect oxidation.

COBALTOUS HYDRATE (SYN. *Cobaltous Hydroxide*). **Formula, Co2HO.**

A blue precipitate produced by potassium or sodium hydrate, in soluble salts of cobalt, which changes colour on boiling.

NICKELOUS HYDRATE (SYN. *Nickelous Hydroxide*). **Formula, Ni2HO.**

A bluish-green precipitate, produced in a similar manner to the above, which does not change colour on boiling.

FERROUS HYDRATE. Formula, Fe2HO.

A dirty-green precipitate produced in solutions of ferrous salts by alkaline hydrates slightly soluble in excess. Exposed to the air, it rapidly changes to ferric hydrate.

FERRIC HYDRATE (SYN. *Ferri Peroxidum Humidum, B.P. Moist Hydrated Peroxide of Iron. Ferric Hydroxide*). **Formula, Fe6HO. Molecular Weight, 214.**

This is a gelatinous brown precipitate, produced by treating a soluble ferric salt with an alkaline hydrate. It is called in the B.P. *ferri peroxidum humidum*, and is prepared by precipitating a solution of ferric sulphate with sodic hydrate :—

$$Fe_23SO_4 + 6NaHO = Fe_26HO + 3Na_2SO_4.$$

When dried at 212° F., ferric hydrate loses water, and is converted into ferric oxy-hydrate, having the composition of $Fe_2O_2.2HO$. This substance is called in the B.P. *ferri peroxidum hydratum*, and is formulated according to old views as ferric oxide with one molecule of water attached, $F_2O_3H_2O$.

It is a reddish-brown powder, destitute of taste, and not magnetic. It dissolves completely, though slowly, without the aid of heat, in hydrochloric

acid diluted with half its volume of water, and this solubility causes its use instead of the actual Fe_2O_3, which is not readily soluble in dilute acids. Heated to dull redness in a test tube, it gives off moisture, and becomes transformed into ferric oxide.

(*For analysis see Author's* **Analytical Chemistry**, *page* 89.)

When freshly precipitated ferric hydrate is kept under water, it decomposes after some time, two molecules changing into a ferric oxy-hydrate, having the composition $Fe_2O_3Fe_26HO$, and water being set free :—

$$2Fe_26HO = Fe_4O_36HO + 3H_2O.$$

When thus altered by exposure, it loses its virtue as an antidote to arsenical poisoning. The freshly-made hydrate is an antidote, from its power of forming an insoluble ferrous arseniate in the stomach.

$$As_2O_3 + 2Fe_26HO = Fe_32AsO_4 + Fe2HO + 5H_2O.$$

Ferric hydrate is readily soluble in fixed organic acids and their acid salts, and the solutions so obtained are not precipitable by ammonium hydrate. It is upon this fact that the manufacture of the **scale preparations** of the B.P. depends.

To make them, freshly precipitated ferric hydrate is dissolved in either citric acid or potassium acid tartrate, and ammonium hydrate having been added, the solution is evaporated to a syrup, and is spread upon glass plates and dried. In this way a soluble, yet neutral, salt is obtained, containing iron in the ferric state, which could not be done without the presence of an organic acid, as, under ordinary circumstances, any attempt to neutralize a ferric salt with ammonium hydrate would cause the formation of insoluble ferric hydrate.

It has been already seen that when ferric hydrate is kept under water or dried *in vacuo*, it becomes changed to the ferric oxy-hydrate, Fe_4O_36HO. If the whole be boiled for some time, a still further loss of water takes place, and a modified ferric oxy-hydrate is produced, having the composition Fe_4O_32HO, and thus resembling the B.P. oxy-hydrate. This *modified ferric hydrate*, as it is called, is nearly insoluble in nitric, and only dissolves with the greatest difficulty in boiling hydrochloric acid. When it is placed in contact with dilute acetic acid, it slowly dissolves, forming a most peculiar liquid, which although appearing perfectly clear when viewed by transmitted light, yet looks turbid in reflected light, and, moreover, refuses to give the dark blue precipitate with potassium ferrocyanide so characteristic of ferric solutions generally. Some chemists have considered that the dilute acid does not really dissolve the modified hydrate, but only suspends it as a sort of emulsion of very finely divided particles, and they thus account for its not yielding prussian blue, and its immediate reprecipitation by a strong acid. When ferric hydrate is dissolved in solution of ferric chloride or ferric acetate, and the whole submitted to dialysis, a dark red fluid remains in the dialyzer, which is highly charged with the hydrate which has been lately introduced as *liquor ferri dialysati*. On boiling down a little, or by adding a trace of sulphuric acid, the liquid immediately coagulates to a dark-red jelly, which is then no longer soluble in water. Alcohol, sugar, and acetic acid may, however, be added to the dialyzed liquid without producing coagulation. It would thus seem that there are really two states of colloidal ferric hydrate, the one soluble and the other insoluble in water. The following natural ferric oxy-hydrates have been definitely analyzed :—

Turgite	Fe_4O_52HO.
Goethite	Fe_4O_44HO.
Limonite and ordinary "rust" . .	Fe_4O_36HO.
Huttenrode ore	Fe_4O_38HO.

FERROUS OXIDE. Formula, FeO.

Is a very unstable oxide, only isolated with difficulty by passing a mixture of carbonic oxide and carbonic anhydride over red-hot ferric oxide. It cannot be prepared from its hydrate.

FERRIC OXIDE (SYNS. *Iron Rust. Hæmatite*). **Formula, Fe_2O_3. Molecular Weight, 160.**

Is the chief part of the red deposit that forms on iron, known as rust. It exists in nature as *hæmatite*, and in many other ores of iron It is produced by heating ferric hydrate to dull redness :—

$$Fe_2 6HO = Fe_2O_3 + 3H_2O.$$

When ferrous sulphate is heated strongly, it first turns white, owing to the formation of the anhydrous salt; then yellow, an oxy-sulphate forming; and lastly, brick-red. The last product is ferric oxide, the formation of which may be represented as follows :—

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

In most instances the Fe_2O_3 contains a small quantity of oxy-sulphate; there are several commercial names for this oxide, such as *jewellers' rouge*, *colcothar*, and *red crocus*. Hæmatite reduced to powder forms *Venetian red*.

After ignition, it is extremely insoluble in acids, and indeed refuses altogether to dissolve in concentrated nitric acid. When heated to redness in a current of hydrogen it is reduced to metallic iron, and water is evolved :—

$$Fe_2O_3 + 3H_2 = Fe_2 + 3H_2O.$$

Ferrum redactum, B.P., is thus made. It is a greyish-black metallic powder, soluble in hydrochloric acid with effervescence, liberating hydrogen. It should be soluble in strong solution of iodine (*liquor Iodi*) ; but very few Samples will stand this test, as they nearly all contain ferroso-ferric oxide, Fe O_4, which is produced by insufficient reduction and is insoluble in *liquor Iodi*.

Ferric oxide is not in the B.P., but its hydrates are included. Iron is usually estimated in the form of ferric oxide.

FERROSO-FERRIC OXIDE (SYN. *Magnetic Oxide of Iron*). **Formula, Fe_3O_4. Molecular Weight, 232.**

Is found in Sweden, and known as *magnetic iron ore*, and also constitutes the black scales which fall off iron when it is being welded. It is a mixture of one molecule of ferrous and the same quantity of ferric oxide. Thus,—

One molecule Ferrous Oxide	FeO
,, Ferric Oxide	Fe_2O_3
,, Magnetic Oxide	Fe_3O_4

According to the B.P., it is prepared by mixing solution of **ferrous** and of **ferric sulphates**, and precipitating with **sodium hydrate**, forming ferroso-ferric hydrate :—

$$FeSO_4 + Fe_2 3SO_4 + 8NaHO = Fe_3 8HO + 4Na_2SO_4.$$

This precipitate, having been washed free from the sodium sulphate, is dried at a temperature of 120° F. :—

$$Fe_3 8HO = Fe_3O_4 + 4H_2O.$$

Ferri oxidum magneticum is a brownish black, destitute of taste, strongly attracted by the magnet. It dissolves, without effervescence, in hydrochloric acid, diluted with half its volume of water.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 92.)

A simple way of making this oxide from ferrous sulphate is to divide the quantity into thirds. Two thirds are to be dissolved in the water, acidulated with sulphuric acid, and then heated with just enough nitric acid to change it to ferric sulphate (*see* **Ferric Sulphate**), carefully avoiding excess. The remaining one third having been dissolved in water, the solutions are to be mixed, and precipitated with excess of *liquor sodæ*. The quantities thus taken are derived from the equation, which shows, that of the total iron used, two atoms are in the ferric and one in the ferrous state.

As prepared by the B P. process the oxide is not pure, but contains traces of ferric oxide, with 20 per cent. of combined water.

STANNOUS HYDRATE (SYNS. *Stannous Hydroxide. Hydrated Oxide of Tin*) **Formula, Sn2HO.**

Is a white precipitate produced by potassium, sodium, or ammonium hydrate, insoluble in excess of ammonium, but soluble in potassium and sodium hydrate. On boiling the solution, a black precipitate of stannous oxide is formed, which serves to distinguish stannous from stannic salts. These latter give, with potassium or sodium hydrate, a white precipitate of stannic acid, soluble in excess, the solution being unaltered on boiling.

STANNOUS OXIDE (SYN. *Protoxide of Tin*). **Formula, SnO. Molecular Weight, 134.**

This is the lowest of the three combinations which tin forms with oxygen, two of which form hydric salts (acids) It is the base of stannous salts.

Stannic Oxide (the base of stannic salts) . . .	SnO_2.
Stannic Sesquioxide	Sn_2O_3.
Stannic Acid (producing stannates of metals) . .	H_2SnO_3.
Meta Stannic Acid	$H_{10}Sn_5O_{15}$

In stannous salts, tin acts as a dyad, while in stannic salts it exhibits its full tetrad atomicity. Alkaline stannates are prepared by fusing stannic oxide with an alkaline hydrate, and are much used by dyers. Meta stannic acid is the white powder produced when tin is treated with strong nitric acid, and is insoluble in all acids, but when treated with alkaline hydrates it yields *metastannates*

1 **Stannous Oxide** is precipitated by boiling a solution of stannous hydrate in excess of potassium hydrate.

2 **Stannic Oxide** is produced, like zinc oxide, when tin is burned in the air at a high temperature, and is produced by heating strongly either stannic or meta stannic acids. *Tutty* (or *putty*) *powder* is indifferently stannic oxide or meta stannic acid, and is used as a polishing powder. Tin is estimated in this form

3 **Stannic Acid** is precipitated by alkaline hydrates from stannic salts, and the precipitate is soluble in excess of the hydrate.

PLUMBIC HYDRATE (SYNS. *Plumbic Hydroxide. Hydrated Oxide of Lead*). **Formula, Pb2HO**

A white precipitate, caused in a soluble salt of lead, by potassium or sodium hydrate, soluble in excess of the precipitants. Ammonium hydrate gives a white precipitate with salts of lead, which is a basic compound, and is not soluble in excess.

PLUMBIC OXIDE (SYNS. *Massicot. Litharge*). **Formula, PbO. Molecular Weight, 223.**

Is prepared by heating lead to a dull redness, in contact with the air. Lead, when thus treated, does not burn like magnesium or zinc, but becomes coated with yellow scales of PbO, which are called *massicot.* These scales, when collected and fused, aggregate, and change to a sort of dull reddish flesh colour, and the oxide is then sold as *litharge.* Like the light and the heavy magnesias, these oxides are similar in chemical constitution, only differing in weight and colour. The solvents for plumbic oxides are dilute nitric or acetic acids, as lead forms insoluble sulphate and nearly insoluble chloride. Lead is usually estimated in this form.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 92.)

TRIPLUMBIC TETROXIDE (SYNS. *Red Lead. Minium*). **Formula, Pb_3O_4 Molecular Weight, 685.**

Is formed by heating *litharge* to a low temperature for several hours, in contact with the air, when it also absorbs oxygen, and becomes a dark red mass, which on being pulverized turns scarlet. The powder thus produced is a mixture of two molecules of plumbic oxide with one molecule of the plumbic peroxide (*hereafter described*), thus :—

2 molecules PbO = Pb_2O_2
1 ,, PbO_2 = PbO_2
1 ,, red lead = Pb_3O_4

When treated with dilute nitric, or other acids having the power of dissolving plumbic oxide, red lead is decomposed, the peroxide portion depositing, while the oxide portion dissolves to form a salt of the acid used. (*See* **Peroxide.**) The only acids capable of entirely dissolving red lead are strong acetic, phosphoric, and arsenic Heated with hydrochloric acid, it is first resolved into plumbic chloride and peroxide; and then the latter is, in its turn, dissolved, with the production of chlorine.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 93.)

PLUMBIC ANHYDRIDE, or PLUMBIC PEROXIDE (SYN. *Puce Oxide of Lead*). **Formula, PbO_2. Molecular Weight, 239.**

By digesting red lead with dilute nitric acid, at a gentle heat, forming at the same time, plumbic nitrate in solution.

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb2NO_3 + 2H_2O$$

The action takes place as completely, although not so rapidly, in the cold. The powder thus produced, when filtered out, washed, and dried, is of a puce brown colour, and is a powerful oxidant. Triturated with phosphorus and many organic substances, such as sugar, tartaric and citric acids, the mixture

takes fire, from the rapidity with which PbO_2 oxidizes these substances. Heated with **hydrochloric acid**, it yields **plumbic chloride** and free **chlorine**:—

$$PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O.$$

(*For analysis, see Author's* **Analytical Chemistry**, *page* 93.)

Besides the above oxides, a suboxide and sesquioxide of lead are known, and the complete list is as follows:—

Plumbous or Suboxide	Pb_2O.
Plumbic Oxide	PbO.
Plumbic Peroxide	PbO_2.
Red Lead	Pb_3O_4.
Sesquioxide	Pb_2O_3.

The suboxide is prepared by heating plumbic oxalate in a closed vessel to a temperature not exceeding 400° F.:—

$$2PbC_2O_4 = Pb_2O + 3CO_2 + CO.$$

BISMUTHOUS HYDRATE (Syns. *Bismuth Hydroxide. Hydrated Oxide of Bismuth*). **Formula, Bi_26HO.**

Is a white precipitate, produced in soluble salts of bismuth by alkaline hydrates, *insoluble in excess of the precipitant.*

BISMUTHOUS OXIDE (Syn. *Oxide of Bismuth*). **Formula, Bi_2O_3. Molecular Weight, 468.**

This is the most important of the four oxides, the first three of which correspond to those of antimony. A dioxide, Bi_2O_2, is possibly the radical *bismuthyl*, BiO, in the free state; though antimonyl (SbO) is not so known. Bismuthous oxide may be procured by heating *Bismuthi Subnitras*, B.P. (bismuthyl nitrate, $BiONO_3$), or by exposing the fused metal to the action of the air. It is a pale yellow powder, fusing at a red heat, solidifying into a yellow transparent mass. Bismuth is estimated in this form.

(*See Author's* **Analytical Chemistry**, *page* 168.)

According to the B.P., *Bismuthi oxidum* is made by digesting **bismuthyl nitrate** (*Bismuthi subnitras*) in solution of **sodium hydrate**. It directs us to mix the ingredients and boil for five minutes, then having allowed the oxide to subside, decant the supernatant liquid, wash the precipitate thoroughly with distilled water, and finally dry the oxide by the heat of a water bath.

Bismuthi oxidum is a dull lemon yellow powder. Heated to redness it becomes deep orange but is not diminished in weight. It is insoluble in water, but soluble in nitric acid mixed with half its volume of water.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 93.)

Besides the impurity of silver (a test for the presence of which is provided by the B.P.), bismuth compounds have been found to contain traces of gold, and also of selenium and tellurium. The former may be detected by heating a little of the compound on a charred match, saturated with sodium carbonate, and held under a cold porcelain plate, when a red film will be formed. Generally it may be taken that any sample of commercial metallic bismuth, which, after dissolving in *aqua regia*, yields a black or red precipitate when excess of sulphurous anhydride is passed through the solution, should not be used for making the official salts (*Schacht*).

BISMUTHIC OXIDE. **Formula, Bi_2O_5.**

Bright red in colour, and acts only as an anhydride.

ANTIMONIOUS OXIDE (SYNS. *Oxide of Antimony. Antimonii Oxidum, B.P. Flores Antimonii. Argentic Flowers of Antimony*). **Formula, Sb_2O_3. Molecular Weight, 292.**

Obtained by precipitating **antimonious chloride** by dilution with **water**, and treating the precipitated oxy-chloride of antimony with **sodium carbonate**. The reaction is: —

$$12SbCl_3 + 15H_2O = 2SbCl_3.5Sb_2O_3 + 30HCl.$$

$$2SbCl_3.5Sb_2O_3 + 3Na_2CO_3 = 6Sb_2O_3 + 6NaCl + 3CO_2.$$

Upon drying the precipitate at a higher temperature than that directed to be employed (212° F.), it forms the higher antimony oxides by union with oxygen derived from the air. These are insoluble in potassium acid tartrate, whereas Sb_2O_3 is readily dissolved in a hot solution of the same.

Antimonii oxidum is a greyish-white *amorphous* powder, fusible at a low red heat, and volatile in a closed vessel, but converted by heating in the air to Sb_2O_4. It is insoluble in water, but readily dissolved by hydrochloric acid, and by *fuming* sulphuric acid. It dissolves entirely when boiled with an excess of potassium acid tartrate.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 93.)

The colour of the precipitate, when prepared from antimony entirely uncontaminated by iron, is pure white. It fuses readily, and is soluble in fuming sulphuric acid. It is also formed when metallic antimony is melted in a crucible, the lid of which only partially excludes the air. It is then produced in a crystalline form, and is readily soluble in alkaline hydrates, forming *antimonites*. Two other oxides of antimony exist, viz., **antimonioso-antimonic oxide**,—

$$Sb_2O_4 \text{ or } (Sb_2O_3.Sb_2O_5) \text{ otherwise } Sb_4O_8,$$

and **antimonic oxide** (antimonic anhydride) Sb_2O_5. The former is occasionally, though incorrectly, denominated antimonious anhydride, this title belonging to Sb_2O_3. It may be obtained by heating either of the other oxides. In one case oxygen is absorbed, in the other it is evolved. Also the action of the nitric acid upon metallic antimony forms Sb_2O_4.

Antimonic oxide may be produced by heating **antimonic hydrate** obtained from the action of **nitric acid** upon **antimony.** The hydrate also results from the addition of water to antimonic chloride, and from the precipitation of potassium or sodium antimoniate by an acid. **Potassium metantimoniate** may be obtained from the metal by the fusion of antimony with potassium nitrate, and acting upon the product by potassium hydrate. It is used in analysis for the precipitation of sodium salts, of which *sodium metantimoniate* is the least soluble.

CHROMIUM forms an extensive list of oxides:—

Chromous Oxide	CrO.
Chromic Oxide	Cr_2O_3.
Chromoso-Chromic Oxide	Cr_3O_4.
Chromic Anhydride	CrO_3.
Perchromic Anhydride	Cr_2O_7.

CHROMIC HYDRATE (SYNS. *Chromic Hydroxide. Hydrated Oxide of Chromium*). **Formula, $Cr_2 6HO$.**

Is a bluish green precipitate, produced by potassium, sodium, or ammonium hydrates, in soluble salts of chromium. It is soluble in excess of the precipitant, if cold, but is entirely deposited on boiling. Chromates and dichromates do not yield this precipitate until reduced to chromic salts by heating with hydrochloric acid and a reducing agent, such as alcohol, sulphurous acid, or sulphuretted hydrogen.

CHROMOUS OXIDE. Formula, CrO.

Has not yet been isolated, as in drying its hydrate, it is decomposed to chromoso-chromic oxide.

CHROMIC OXIDE. Formula, Cr_2O_3.

Prepared—

1. By calcining chromic hydrate.
2. By calcining one molecule of potassium dichromate, with a molecular weight of sulphur:—

$$2K_2Cr_2O_7 + S_2 = 2Cr_2O_3 + 2K_2SO_4;$$

and dissolving out the potassium sulphate from the insoluble oxide.

Chromic oxide is a green substance, which when carefully prepared will dissolve in acids, but when heated to redness, a sudden incandescence runs through the mass, and it is then insoluble in both acids and alkalies. When fused with alkalies in contact with the air, it forms a chromate of the alkali employed.

CHROMOSO-CHROMIC OXIDE. Formula, Cr_3O_4.

Prepared by drying chromous hydrate in the air. It is a snuff-brown substance, strongly magnetic.

CHROMIC ANHYDRIDE (SYN. *Chromic Acid*). **Formula, CrO_3.**

Prepared, with difficulty, by decomposing chromium fluoride with water. It is also prepared by decomposing a saturated solution of potassium dichromate with sulphuric acid:

$$K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O.$$

The chromic anhydride crystallizes out on cooling, in brilliant, dark-red needles. It is a powerful oxidizer, and when set free from a mixture of potassium dichromate and sulphuric acid, is used for that purpose in the B.P. preparation of valerianic acid. When mixed with combustible bodies it is reduced to the basylous state, sometimes so quickly as to cause the body with which it is mixed to burst into flame. It forms a series of salts called **chromates**, having for their acidulous radical CrO_4, acting as a dyad. By the action of acids, these salts yield dichromates, having an extra molecule of chromic anhydride, CrO_3. The acid radical of dichromates may therefore be written Cr_2O_7, acting as a dyad. The chromates of the alkalies are soluble, while those of the other metals are chiefly insoluble. All of the salts of chromic acid have very brilliant colours, and are exceedingly poisonous.

POTASSIUM CHROMATE. Formula, K_2CrO_4, and

POTASSIUM DICHROMATE. Formula, $K_2Cr_2O_7$. Molecular Weight, 295.

Are prepared, the one after the other, like manganates and permanganates, by fusing *chrome iron ore*, $FeCr_2O_4$, with potassium nitrate, in contact with the air. In practice, however, the nitrate is now dispensed with, and the chrome ore is simply heated with potassium carbonate, in contact with the oxygen of the air, in a reverberatory furnace, the powder being mixed with calcium oxide to prevent it fusing, and to form a spongy mass, which more readily absorbs the oxygen :—

$$4FeCr_2O_4 + 8K_2CO_3 + 7O_2 = 8K_2CrO_4 + 2Fe_2O_3 + 8CO_2.$$

The mass is then treated with water, which dissolves out the potassium chromate, producing a bright yellow solution. This, when acidulated with sulphuric acid, turns orange, and on evaporation deposits crystals of potassium dichromate, -

$$2K_2CrO_4 + 2H_2SO_4 = K_2Cr_2O_7 + 2KHSO_4 + H_2O.$$

The B.P. thus describes *Potassæ bichromas* :—

In large, red, transparent, four-sided tables, anhydrous; fuses below redness; at a higher temperature is decomposed, yielding green oxide of chromium and yellow chromate of potash, which may be separated by dissolving the latter in water. If dissolved in water, and the solution digested with sulphuric acid and rectified spirit, it acquires an emerald-green colour.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 94.)

If potassium dichromate be heated with sulphuric acid and sodium chloride, a product is formed having the formula CrO_2Cl_2, which is termed chromyl chloride, or (improperly) chlorochromic acid. It is produced thus :—

$$K_2Cr_2O_7 + 3H_2SO_4 + 4NaCl = 2CrO_2Cl_2 + K_2SO_4 + 2Na_2SO_4 + 3H_2O.$$

It is decomposed by water into chromic and hydrochloric acids; but by the action of hydrates, salts may be formed, which are yellow or orange in colour.

(*For tests for Chlorine in the presence of Bromides, see Author's* **Analytical Chemistry**, *page* 51.)

Chromyl chloride, which is also frequently known as chlorochromic anhydride, forms no salt of pharmaceutical value. Potassium dichromate is a powerful direct oxidizer, and in presence of excess of acid it raises iron from the ferrous to the ferric state. One molecule of this salt has the power to convert six molecules of a ferrous salt in this manner. Thus with ferrous chloride and hydrochloric acid :—

$$6FeCl_2 + 14HCl + K_2Cr_2O_7 = 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O.$$

Or with sulphate and sulphuric acid :—

$$6FeSO_4 + 7H_2SO_4 + K_2Cr_2O_7 = 3Fe_23SO_4 + Cr_23SO_4 + K_2SO_4 + 7H_2O.$$

It is, therefore, used in the B.P. for the volumetric estimation of iron.

(*See Author's* **Analytical Chemistry**, *page* 158.)

ARGENTIC CHROMATE. Formula, Ag_2CrO_4.

A bright carmine-red precipitate obtained by treating a neutral solution of **argentic nitrate** with **potassium chromate**. It is used as an *indicator* in the volumetric analysis of soluble chlorides, because it will not form until the whole of the chlorine present has been precipitated as argentic chloride.

PLUMBIC CHROMATE (SYN. *Chrome Yellow*). **Formula, $PbCrO_4$.**

Is found native under the mineralogical name of *crocoïsite.* It is produced by precipitating a **soluble salt of lead** with **potassium chromate.** It is insoluble in water, and only very slightly so in dilute acids. It is, however, rapidly dissolved by solution of potassium hydrate. Digested with strong hydrochloric acid, it yields a deep red liquid which smells strongly of chlorine, and possesses the power of dissolving gold. (*See* **Chromic Chlorides.**) The use of excess of the lead salt in the manufacture of chrome yellow causes the formation of *orange chrome.*

BISMUTHOUS CHROMATE. Formula, Bi_23CrO_4.

A yellow precipitate produced by treating a solution of a soluble bismuthous salt with potassium chromate. It is readily soluble in dilute nitric acid.

PERCHROMIC ANHYDRIDE. Formula, Cr_2O_7.

Is a deep-blue liquid caused by the action of hydric peroxide upon chromic acid.

(*See Author's* **Analytical Chemistry,** *page* 73.)

CHAPTER VII.

SULPHUR AND ITS COMPOUNDS.

SULPHUR (SYNS. *Sulphur Vivum. Brimstone*). **Symbol, S. Atomic Weight, 32. In the free state, S_2 or S_6.* Vapour Density,** *referred to air*, **2·22. Vapour Density,** *referred to Hydrogen*, **32.**

This element is found native in the free state, in yellow masses, having a crystalline structure. It is also extensively spread over the earth, combined with metals, in the form of pyrites and similar sulphides. It exists in animal tissues, urine, blood, and in the volatile oils of many plants, especially those of the *Allium*, or onion class. Free native sulphur is chiefly found in the volcanic regions of Italy, Sicily, and Mexico. It is purified by distillation in rude earthen pots, placed in a furnace, and communicating with similar pots, outside the furnace, from which the distilled sulphur runs into water. As thus obtained, it is in masses, called **rough** sulphur.

These masses are further purified by redistillation, or sublimation, to form the various commercial varieties, which are as follows :—

1. **Roll Sulphur**, prepared by conveying the vapour from the retorts into a receiver, so heated that the distillate is retained in a state of fusion, whence it is cast into moulds to solidify.

2. **Sublimed Sulphur**, produced when the vapour from the retorts is allowed to pass into a large cool chamber, on the walls of which the sulphur collects as a sublimate. This is the B.P. *Sulphur Sublimatum*, which is thus described :—

A slightly gritty powder, of a fine greenish-yellow colour, without taste, and without odour, unless heated; burning in open vessels with a blue flame, and the evolution of sulphurous anhydride. Entirely volatilized by heat, and when examined under the microscope is seen to be crystalline.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 97.)

Sulphur may also be prepared by heating *iron pyrites* in a closed retort, when part of the sulphur is liberated, and distils over, a residue of **ferroso-ferric sulphide** being left in the retort :—

$$3FeS_2 = Fe_3S_4 + S_2.$$

Native sulphur does not as a rule contain arsenic, but that obtained from *pyrites* is frequently contaminated by **arsenious sulphide** (As_2S_3).

Sulphur is fusible, and volatile without change, in the absence of oxygen; but when heated in contact with the air, it takes fire, and produces **sulphurous anhydride.** In the native state, or when deposited from its solution in carbon disulphide, it crystallizes in octahedra (diamond shape) ; but when fused and cooled, it crystallizes in prisms (needle shape). It is a very pretty experiment

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* At 1832° F. sulphur vapour has the specific gravity which it should have, if we regard its recognised atomic weight. At 932° F., however, its density is three times as great, thus making its molecule S_6, as above.

to melt some sulphur in a covered crucible, and then set it on a stone to cool for a few minutes. Before it is quite cold, the crust at the top is to be broken, and the sulphur which still remains fluid having been poured out, the inside of the crucible will be found incrusted with magnificent needles of crystallized sulphur. Another very interesting experiment is to heat some sulphur in a tube, into which a thermometer has been introduced, and watch the effects. At 234° F. it becomes a straw yellow liquid, as thin as water. At 482° F. it thickens, and becomes a brownish-red plastic mass; and this thickening continues, so that the tube may even be inverted without its contents running out, until the temperature touches 788° F., when it again becomes fluid, and finally boils at 814° F., giving a red vapour having a density of 6·5 (referred to air). Sulphur is soluble in turpentine and carbon disulphide, and slightly so in alcohol. There is, however, a variety called **plastic sulphur,** which is not soluble in these menstrua. It is prepared by melting sulphur till it begins to thicken, and suddenly pouring into cold water. This curious modification is elastic and tenacious, but quickly passes back into ordinary sulphur by exposure to the air for an hour or two. During the conversion of plastic into ordinary sulphur, which takes place rapidly at 212° F., a large amount of latent heat is evolved, and the thermometer instantly rises to 230° F. From these facts it is apparent that sulphur, like oxygen, is an allotropic body. There exists still another variety of sulphur, which is entirely amorphous, viz. :

SULPHUR PRECIPITATUM, B.P. (SYNS. *Lac Sulphuris. Milk of Sulphur.*)

Is prepared by boiling **sulphur** with **calcium hydrate** and **water,** when it dissolves, forming a deep red solution of calcium pentasulphide and calcium hyposulphite :—

$$3Ca2HO + 6S_2 = 2CaS_5 + CaS_2O_3 + 3H_2O.$$

The solution, having been filtered, is treated with **hydrochloric acid,** which forms calcium chloride, and deposits *sulphur precipitatum* :—

$$2CaS_5 + CaS_2O_3 + 6HCl = 6S_2 + 3CaCl_2 + 3H_2O.$$

By many chemists a more complicated view is taken than is expressed in the equation. It is supposed that the hydrochloric acid decomposes the pentasulphide, partially giving off sulphuretted hydrogen, and depositing sulphur :—

$$4CaS_5 + 8HCl = 4CaCl_2 + 8S_2 + 4H_2S.$$

At the same time, it acts on the hyposulphite, to form sulphur and sulphurous anhydride :—

$$2CaS_2O_3 + 4HCl = 2CaCl_2 + S_2 + 2SO_2 + 2H_2O.$$

These two reactions taking place simultaneously, the sulphuretted hydrogen and sulphurous anhydride, instead of being entirely evolved, react upon each other, and deposit the whole of their sulphur :—

$$4H_2S + 2SO_2 = 4H_2O + 3S_2.$$

It is also possible to regard the reaction as a combination of sulphur with **calcyl,** CaO, thus :—

$$2Ca2HO + S_2 = 2CaOS + 2H_2O.$$

And the subsequent decomposition of this body by hydrochloric acid, forming **water, calcium chloride, and sulphur, thus :—**

$$2CaOS + 4HCl = S_2 + 2CaCl_2 + 2H_2O.$$

This is considerably the simplest manner of representation. How far it is

correct, cannot be yet thoroughly determined. It will be seen that the mode of formation resembles that of calcyl chloride. (*See* **Calx Chlorata**, B.P.)

Sulphur precipitatum is a greyish-yellow, soft powder, free from grittiness and from the smell of sulphuretted hydrogen. When heated in an open vessel, it burns with a blue flame and the evolution of sulphurous acid gas. Entirely volatilized by heat, showing absence of calcium sulphate. Under the microscope it is seen to consist of opaque globules without any admixture of crystalline matter, also showing absence of calcium sulphate and sublimed sulphur.

(*For analysis see Author's* **Analytical Chemistry**, *page* 97.)

It is still a common custom of trade to make this substance by the old London formula of 1721, *i.e.*, by using sulphuric instead of hydrochloric acid as the precipitant. This causes the formation of calcium sulphate, which, being nearly insoluble in water, deposits with the sulphur, causing an adulterated product of considerable profit to the manufacturer. Public opinion, it must be admitted, is in favour of the appearance of this article.

The B.P. test of burning on the point of a knife is sufficient to detect the adulteration; but to ascertain its quantity, a weighed portion of the sample should be ignited in a tared porcelain crucible, and the residue again weighed, and its weight calculated to that of crystallized calcium sulphate by the formula—

$$\frac{\text{Residue} \times 172}{136} = \text{amount of } CaSO_4 2H_2O \text{ in the sample.}$$

Sulphur combines directly with basylous radicals to form salts called **sulphides.** They are, with the exception of the alkaline and earthy sulphides, chiefly insoluble in water; and a large number of them are found native.

A remarkable analogy exists between sulphides and oxides, an instance of which may be seen by comparing the equation just given for the manufacture of sulphur from pyrites with that for the production of oxygen from manganic dioxide by heat.

$$3FeS_2 = Fe_3S_4 + S_2.$$
$$3MnO_2 = Mn_3O_4 + O_2.$$

But it is not in such similarity in their reactions alone that the close relationship of sulphur and oxygen are apparent, because we find that the former, acting as a dyad, can displace the latter from its compounds atom for atom. The class of bodies thus formed are called *sulpho-salts*, and correspond in formulæ to the ordinary oxy-salts, but with S displacing O. The following table will make the matter clear:—

Hydrogen Oxide, H_2O, corresponds to H_2S, Hydrogen Sulphide.
Ammonium Hydrate, NH_4HO, corresponds to NH_4HS, Ammonium Sulphydrate.
Ethyl Hydrate, C_2H_5HO, corresponds to C_2H_5HS, Ethyl Sulphydrate.
Carbon Dioxide, CO_2, corresponds to CS_2, Carbon Disulphide.
Sodium Arsenite, Na_3AsO_3, corresponds to Na_3AsS_3, Sodium Sulpharsenite.
Disodium Hydr' Antimonite, Na_2HSbO_3, corresponds to Na_2HSbS_3, Disodium Hydro-Sulphantimonite.

METALLIC SULPHIDES.

HYDROGEN SULPHIDE (SYNS. **Sulphuretted Hydrogen.** *Hydro-Sulphuric Acid. Sulphydric Acid*) **Formula, H_2S. Molecular Weight, 34. Density,** *referred to Hydrogen*, **17. Density,** *referred to Air*, **1·178.**

This is a colourless, invisible gas, having the most disagreeable odour of rotten eggs. It corresponds in formula to water, with the O displaced by S, and may be produced by burning hydrogen in the vapour of sulphur:—

$$\begin{array}{ccccc} 2H_2 & + & S_2 & = & 2H_2S. \\ 4 \text{ vols.} & + & 2 \text{ vols.} & = & 4 \text{ vols.} \end{array}$$

It is found in many mineral waters, notably those of Harrowgate, in Yorkshire, and Moffat, in Scotland, such waters being termed *hepatic*. In practice it is prepared by acting on ferrous sulphide with dilute sulphuric acid:—

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

Or by heating native antimonious sulphide with strong hydrochloric acid:—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The former process is the common one in use in laboratories; but the latter, although more expensive, is very suitable for occasional use, as the moment the source of heat is withdrawn, the evolution of the gas, and consequently the attendant smell, ceases.

When inflamed in a free supply of air, it burns with a lambent flame, forming sulphurous anhydride and water,—

$$2H_2S + 3O_2 = 2SO_2 + 2H_2O.$$

By cold and pressure it can be liquefied, and by extreme cold it may be rendered solid. It is very soluble in water, and the saturated solution which is used in analysis is prepared by passing the gas into water until absorption ceases. One pint of water will dissolve about three pints of the gas. The solution, if exposed to the air, does not keep well, but becomes milky, owing to the deposit of its sulphur,—

$$2H_2S + O_2 = 2H_2O + S_2;$$

and thus it must be freshly made when required for use.

The hydrogen of this acid may be replaced, either entirely or partly, by metals, giving rise to sulphides or sulphydrates, corresponding to oxides and hydrates; thus—

$(NH_4)_2S$ = Ammonium Sulphide.

NH_4HS = Ammonium Sulphydrate.

Seeing that sulphydrates bear a great resemblance to hydrates, and that H_2S_2 (hydrosulphyl) has, like hydroxyl, been obtained in the free state; it follows that HS may form the radical of sulphydrates. With this idea in view, it has been proposed to term sulphydrates "sulphy*lides*." This name, however, does not appear to have any great recommendation in its favour, as a slight clerical error might convert it into sulphide; and its adoption would require that hydrates should be called "hydroxy*lides*." Sulphydrates might however be called "sulphydrides."

With many metals sulphuretted hydrogen forms insoluble precipitates, a fact of great use in analysis, as it serves to divide the metals into four groups, as follows:—

SULPHURETTED HYDROGEN REACTIONS.

I.	II.	III.	IV.
Metals precipitable by H_2S in presence of an acid (HCl), and also by H_2S in presence of an alkali (*i.e.*, insoluble in NH_4HS). Silver Mercury Lead Bismuth Copper } *Black.* Cadmium—*Yellow.*	Metals precipitated by H_2S in presence of HCl, but not in presence of an alkali (*i.e.*, soluble in NH_4HS). Antimony—*Orange.* Tin—*Brown* or *Yellow.* Gold Platinum } *Black.* Also the Metalloid Arsenic —*Yellow.*	Metals not affected by H_2S in presence of HCl, but precipitated in presence of an alkali (*i.e.*, by NH_4HS). Iron Nickel Cobalt } *Black.* Zinc—*White.* Manganese—*Flesh Coloured.* ——— The following are also precipitated by NH_4HS, but not as Sulphides. Aluminium—*White Hydrate.* Chromium—*Green Hydrate.*	Metals not affected by H_2S, either in acid or alkaline solutions. Calcium. Barium. Magnesium. Ammonium. Potassium. Sodium. Lithium.

(*For further information, see Author's* **Analytical Chemistry**, *Chapter II.*)

Equations for all these reactions should be drawn by the student like the following examples :—

1. With a monad metal :—

$$2AgNO_3 + H_2S = Ag_2S + 2HNO_3.$$

2. With a dyad metal :—

$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

3. With a triad metal :—

$$2Bi3NO_3 + 3H_2S = Bi_2S_3 + 6HNO_3.$$

4. In presence of an alkali (*i.e.*, with NH_4HS):—

$$FeSO_4 + NH_4HS = FeS + NH_4HSO_4.$$

Sulphuretted hydrogen is decomposed by all oxidizing agents, whether direct or indirect, the reaction being attended by the deposit of sulphur. Thus with chlorine, bromine, or iodine, an acid is formed and sulphur deposited :—

$$2H_2S + 2Cl_2 = 4HCl + S_2.$$

With potassium chromate or dichromate in the presence of an acid, sulphur is deposited, and the solution becomes green, owing to the formation of a salt of chromium :—

$$2K_2CrO_4CrO_3 + 16HCl + 6H_2S = 2Cr_2Cl_6 + 4KCl + 3S_2 + 14H_2O.$$

In the same way potassium permanganate is decolorized, with the deposition of sulphur, and likewise ferric salts are reduced to ferrous, also with precipitation of sulphur :—

$$2Fe_2Cl_6 + 2H_2S = 4FeCl_2 + 4HCl + S_2.$$

Sulphurous anhydride itself is deoxidized by sulphuretted hydrogen :—

$$SO_2 + 2H_2S = 2H_2O + S_3.$$

AMMONIUM SULPHIDE. **Formula, $(NH_4)_2S$.**

Prepared by dividing some ammonium hydrate into two equal parts. Sulphuretted hydrogen is passed through one portion until absorption ceases, and the liquids are mixed. The solution thus obtained has a faint greenish-yellow colour and a disgusting smell of ammonia gas and rotten eggs. Exposed to the light, it quickly becomes yellow, and changes to **ammonium sulphydrate,** NH_4HS. This latter is the usual laboratory solution, and it is tolerably permanent; but by a few months' exposure it changes to higher sulphides, and then becomes entirely decomposed into ammonic sulphite and sulphate, and deposits sulphur. It is used when sulphuretted hydrogen is to be employed in an alkaline solution. Several sulphides, notably those of arsenic and antimony, are soluble in this solution, forming ammonium sulpharsenite or sulphantimonite, and evolving sulphuretted hydrogen :—

$$As_2S_3 + 6NH_4HS = 2(NH_4)_3AsS_3 + 3H_2S.$$
$$Sb_2S_3 + 6NH_4HS = 2(NH_4)_3SbS_3 + 3H_2S.$$

This property distinguishes As, Sb, Sn, Au, and Pt from all other metals precipitable by sulphuretted hydrogen in an acid solution, the remainder being insoluble in ammonium sulphydrate. Acids decompose the solution of sulphydrate with liberation of sulphuretted hydrogen. It should not give any visible reaction with magnesium sulphate added in excess, showing the absence of free ammonium hydrate. The direct combination of ammonia gas and sulphuretted hydrogen takes place when mixed gases are cooled to about 0° F., the salt being obtained in colourless crystals. These may be volatilized or dissolved without decomposition, and are not formed if the temperature of the mixture be reduced to below 0° F. If the ammonia gas be in excess, ammonium sulphide results (provided the temperature be below 0° F.), also forming colourless crystals, which, if raised slightly in temperature, decompose into ammonium sulphydrate and ammonia gas.

POTASSIUM SULPHIDE (SYNS. *Potassa Sulphurata. Liver of Sulphur*).

Potassium forms five distinct compounds with sulphur, K_2S, K_2S_2, K_2S_3, K_2S_4, K_2S_5. The Pharmacopœia compound, *potassa sulphurata*, is an indefinite mixture of these compounds, according to the amount of sulphur and degree of heat employed. It is prepared by fusing sulphur with potassium carbonate. If the heat be moderate, the B.P. proportions will act somewhat as follows :—

$$3K_2CO_3 + 4S_2 = 2K_2S_3 + K_2S_2O_3 + 3CO_2,$$

forming potassium trisulphide and hyposulphite; but if a stronger heat be applied, the latter salt is decomposed, and we have a mixture of sulphide and sulphate :—

$$4K_2CO_3 + 5S_2 = 3K_2S_3 + K_2SO_4 + 4CO_2.$$

The substance is, however, never definite, and usually contains undecomposed potassium carbonate. It is best to put a small quantity of the mixed

potassium carbonate and sulphur into the crucible at the commencement of the process. When this is fused, and not before, a larger quantity is added; and thus successive portions are treated until the whole is in a state of tranquil fusion. The moment the whole is cooled and solidified, it is broken up, and transferred into previously heated wide-mouthed bottles.

Good *potassa sulphurata* should be in solid greenish fragments, externally liver-brown when recently broken, alkaline and acrid to the taste, forming a yellow solution with water, which has the odour of sulphuretted hydrogen, and evolves it freely on dropping into it excess of hydrochloric acid, sulphur being deposited.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 97.)

When exposed to the air, *liver of sulphur* becomes moist and greenish, owing to the oxidation of the sulphide to hyposulphite and sulphite, and finally an inert white mass is left, containing nothing but potassium sulphate with a few impurities, such as undecomposed carbonate and deposited sulphur. The B.P. supposes that liver of sulphur is usable so long as it contains three-fourths of its weight of K_2S_3, ascertained by extraction with spirit, in which that substance is soluble, while carbonates and sulphates are not affected.

ARGENTIC SULPHIDE. Formula, Ag_2S. Molecular Weight, 248.

Is found native as *silver-glance* or *argentine*, and may be formed by fusing silver with an excess of sulphur. When precipitated from silver solutions by sulphuretted hydrogen it is a blackish powder, insoluble in dilute acid and alkalies; but soluble in strong boiling nitric acid, sulphur being deposited. It is also insoluble in potassium cyanide.

ZINC SULPHIDE. Formula, ZnS. Molecular Weight, 97.

Found native as *blende*, and cannot be formed by direct fusion of zinc and sulphur. When precipitated from a solution of zinc by ammonium sulphydrate, it is a white substance readily soluble in dilute acids, and oxidizing rapidly by exposure to the air. It is not precipitable by sulphuretted hydrogen in the presence of hydrochloric acid, neither is it soluble in dilute acetic acid, which latter property enables us to distinguish it from manganous sulphide.

CADMIUM SULPHIDE (SYN. *Jaune brillant*). **Formula, CdS. Molecular Weight, 144.**

Is found in Scotland as *Greenockite*, and only formed with difficulty by direct fusion of the metal and sulphur. When precipitated by sulphuretted hydrogen in the presence of very dilute hydrochloric acid, it is yellow; and on being filtered out and heated to redness, it turns first brown and finally red. It is easily soluble in boiling strong hydrochloric acid, and in nitric acid. In the first case sulphuretted hydrogen is copiously evolved, and in the second sulphur is deposited. Cadmium sulphide is insoluble in ammonium sulphydrate, which serves to distinguish it from arsenious and stannous sulphides. It is, however, soluble in ammonium hydrate.

CUPROUS SULPHIDE. Formula, Cu_2S.

Occurs as a constituent of *copper pyrites*, $Cu_2SFe_2S_3$, and native as *copper glance*. It may be formed artificially by triturating finely-divided copper with the proper proportion of precipitated sulphur in a warm mortar, when the heat evolved is so great that the whole mass becomes red-hot. By digestion with

dilute and cold nitric acid it is partly dissolved, and partly changed to cupric sulphide.

CUPRIC SULPHIDE. Formula, CuS. Molecular Weight, 95·5.

Found as *indigo copper*, or *blue copper*. When precipitated from a solution of copper by sulphuretted hydrogen it is brownish black, and is insoluble both in dilute acids and in alkaline sulphides, but rapidly dissolved by strong heated nitric acid, and slowly by concentrated hydrochloric acid. It very rapidly oxidizes on exposure to the air, forming cupric sulphate. As it is very slightly but still distinctly soluble in ammonium sulphydrate, it is better to use sodium sulphide for the separation of the metals of the second group, when the presence of a small trace of copper is suspected.

MERCUROUS SULPHIDE. Formula, Hg_2S.

It is doubtful whether this body really exists as a definite compound, some chemists preferring to view it as a mixture of mercuric sulphide and mercury. It is precipitated from solution of mercurous salts by sulphuretted hydrogen.

MERCURIC SULPHIDE. Formula, HgS. Molecular Weight, 232.

Is known in two forms—a red and a black. The red variety is found native as *cinnabar*, and when it has been reduced to a very fine state of division it constitutes the beautiful red pigment called vermilion. In the black form it is produced either by triturating mercury with sulphur or precipitating a mercuric solution by excess of sulphuretted hydrogen. In the latter case it is a black powder, insoluble even in boiling nitric acid, and also in hydrochloric. It is, however, attacked when heated with concentrated sulphuric acid, with formation of mercuric sulphate and evolution of sulphurous anhydride, and it is also dissolved by nitro hydrochloric acid, producing mercuric sulphate. The product which is obtained by rubbing mercury with excess of sulphur, is known as **ethiops mineral**, and was formerly official as *hydrargyri sulphuretum cum sulphure*.

Vermilion may be prepared by subliming the ethiops mineral and triturating the sublimate till the red colour is properly developed. A more practical process is to triturate the "ethiops" with heated solution of potassium hydrate for several hours, when it gradually changes to the required colour.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 95.)

MANGANOUS SULPHIDE. Formula, MnS. Molecular Weight, 87.

Occurs native as *manganese blende*, and is formed as a flesh-coloured precipitate on adding ammonium sulphydrate to a soluble salt of manganese. It is distinguished from the sulphides of cobalt, nickel, and zinc, by being soluble in acetic acid.

FERROUS SULPHIDE (SYN. *Iron Monosulphide*). **Formula, FeS.** *Iron*, 63·63; *Sulphur*, 36·37; total, 100·00. **Molecular Weight, 88.**

Is prepared by mixing together iron filings and sulphur, and projecting the mixture, a little at a time, into a very bright red-hot crucible. According to the B.P., it is prepared by heating an iron rod to whiteness in a smith's forge, and pressing a roll of sulphur against it, when the sulphide forms in fused masses, which are allowed to drop into a pail of water. Adopting this latter

process, it can be prepared with extreme facility; it then appears as small, shiny, variously-shaped nodules. The great use of the ferrous sulphide thus formed is for making sulphuretted hydrogen. When precipitated from a solution of iron by ammonium sulphydrate it is a black powder, very readily soluble in *cold* dilute hydrochloric acid, by which means it may be separated from cobaltous and nickelous sulphides. It is not formed by sulphuretted hydrogen in the presence of hydrochloric acid, and it readily oxidizes in contact with the air.

FERRIC SULPHIDE (SYN. *Iron Sesquisulphide*). **Formula, Fe_2S_3.** *Iron,* 53·85; *Sulphur,* 46·15; total 100·00.

Is produced when *iron pyrites* are heated to dull redness; it exists also in *copper pyrites.* (Iron, 30·6; sulphur, 34·9; copper, 34·5.)

The term *pyrites* is applied to various substances more or less chemically allied, but possessing this point in common, that their principal constituents should be sulphur, combined with either iron or copper.

FERRIC DISULPHIDE (SYN. *Pyrites* [*par excellence*]). **Formula, FeS_2.** *Iron,* 46·67; *Sulphur,* 53·33; total, 100·00.

Is found native as *yellow iron pyrites.* When roasted with a free access of air it evolves sulphurous anhydride, and leaves a residue of ferric oxide. Distilled in a closed vessel, sulphur passes over, and a residue of *magnetic pyrites,* Fe_3S_4, remains, which becomes rapidly converted into ferrous sulphate by exposure to the air.

COBALTOUS SULPHIDE. Formula, CoS; and

NICKELOUS SULPHIDE. Formula, NiS.

Both are black, and precipitated from solutions of their respective metals by ammonium sulphydrate, but not by sulphuretted hydrogen in the presence of hydrochloric acid. They are insoluble in cold dilute hydrochloric acid (distinction from FeS).

STANNOUS SULPHIDE. Formula, SnS. Molecular Weight, 150.

A brown precipitate produced in solutions of *stannous* salts by sulphuretted hydrogen in the presence of hydrochloric acid. It is soluble in ammonium sulphydrate; and on the addition of hydrochloric acid the solution deposits stannic sulphide, owing to the presence of excess of sulphur in most samples of the sulphydrate.

STANNIC SULPHIDE. Formula, SnS_2. Molecular Weight, 182.

Separates when a *stannic* solution is treated with sulphuretted hydrogen in the presence of hydrochloric acid, as a yellow precipitate. It is soluble in ammonium sulphydrate, and reprecipitated on the addition of hydrochloric acid. It dissolves in boiling strong hydrochloric acid, while arsenious sulphide does not, and the solution treated with a fragment of pure zinc in a platinum dish deposits a granular mass of metallic tin.

BISMUTHOUS SULPHIDE. Formula, Bi_2S_3. Molecular Weight, 516.

Forms when a soluble bismuthous salt is precipitated by sulphuretted hydrogen. It is insoluble in hydrochloric acid and ammonium sulphydrate,

but soluble in nitric acid. It occurs native as *bismuth glance*, and may be prepared by fusing the metal with sulphur.

ANTIMONIOUS SULPHIDE (SYN. *Black Antimony*). **Formula, Sb_2S_3. Molecular Weight, 340.**

Found native, and sold as *black antimony;* also produced in the form of an orange precipitate, when a solution of antimony is treated with sulphuretted hydrogen in the presence of an acid. The precipitated sulphide when heated becomes black, and aggregates, proving that the two are simply different forms of the same substance. The native antimonious sulphide, when fused, forms the so-called *crude antimony*, and bears a great resemblance to metals. By ignition in the air it becomes partially transformed into oxide, forming a light powder, termed *antimony ash*. By fusing this in a Cornish or Hessian crucible, *antimonial glass* is formed. The insoluble part of the product obtained by submitting a mixture of antimonious sulphide and potassium nitrate to a red heat, is known as *antimonial crocus*, or *saffron of antimony*, and the entire residue after lixiviation, as *liver of antimony*.

To avoid using the black antimony, the B P. has a process for dissolving it, and getting it into the orange form by reprecipitation. In this state it is more sightly, and in an infinitely finer state of division than could ever be obtained by powdering. The product, however, is not one of perfect purity or definite composition. It is called **antimonium sulphuratum** (SYN. *Antimonii Oxysulphuretum, Lond.*), and is prepared as follows.—

Black antimony is boiled with *liquor sodæ* for two hours. The liquor is strained through calico, and before it cools, diluted sulphuric acid is added to it by degrees till the latter is in slight excess. The precipitate is washed till free from sulphates and dried at a temperature not exceeding 212°.

Thus made, *antimonium sulphuratum* is an orange red powder, containing sulphide of antimony, Sb_2S_3, with a small and variable amount of oxide of antimony, Sb_2O_3. It is readily dissolved by caustic soda, also by hydrochloric acid with the evolution of sulphuretted hydrogen and the separation of a little sulphur.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 98.)

In the above process, the sodium hydrate is supposed to dissolve the native sulphide, forming sodium sulphantimonite in solution, together with sodium antimonite:—

$$Sb_2S_3 + 6NaHO = Na_3SbS_3 + Na_3SbO_3 + 3H_2O.$$

These salts dissolve an indefinite quantity of antimonious sulphide, which would be deposited out on cooling, to prevent which sulphuric acid is added, which causes decomposition, and a deposit of orange antimonious sulphide, together with a variable proportion of oxide, derived from the antimonite formed in the first reaction:—

$$2Na_3SbS_3 + 2Na_3SbO_3 + 6H_2SO_4 = Sb_2S_3 + Sb_2O_3 + 6Na_2SO_4 + 3H_2O + 3H_2S.$$

Sulphuric acid is used because the product is not so readily soluble in excess of that acid as in hydrochloric; moreover, the employment of the latter body would have a tendency to cause the formation of an oxychloride.

Antimonium sulphuratum is commonly known as *kermes mineral*, and many commercial samples contain free sulphur as well as oxide. This may be proved and its amount estimated by digesting the carefully dried sample in carbon disulphide, and evaporating the solution thus obtained to dryness, and weighing the residue. The oxide is best extracted by digestion in tartaric acid, in which it is soluble.

When antimonious sulphide is produced by precipitation from a soluble antimonious salt with sulphuretted hydrogen, it is a bright orange substance, insoluble in dilute, but freely soluble in strong hydrochloric acid, with evolution of sulphuretted hydrogen. The solution thus obtained, when introduced into a platinum vessel with a fragment of pure zinc, causes a black deposit of antimony to form as a *closely adherent* coating on the platinum. Antimonious sulphide is freely soluble in ammonium sulphydrate, and is reprecipitated on supersaturation with dilute hydrochloric acid.

ANTIMONIC SULPHIDE. Formula, Sb_2S_5.

Is produced by acting on antimonic chloride by sulphuretted hydrogen. It is orange-yellow, and dissolves in boiling hydrochloric acid, with evolution of sulphuretted hydrogen and deposition of sulphur. It is also soluble in ammonium sulphydrate, and is contained in many commercial samples of *kermes mineral.* A mixture of the two sulphides is known as *golden sulphide of antimony.*

COMPOUNDS OF SULPHUR WITH OXYGEN.

Sulphur forms with oxygen two oxides and several acids, as follows :—

Hyposulphurous Acid, H_2SO_2.			
Sulphurous Anhydride, SO_2,	forming Sulphurous	Acid,	H_2SO_3.
Sulphuric Anhydride, SO_3	„ Sulphuric	Acid,	H_2SO_4.
	Thiosulphuric	„	$H_2S_2O_3$.
	Dithionic	„	$H_2S_2O_6$.
	Trithionic	„	$H_2S_3O_6$.
	Tetrathionic	„	$H_2S_4O_6$.
	Pentathionic	„	$H_2S_5O_6$.

HYDROGEN HYPOSULPHITE (SYNS. *Hyposulphurous Acid. Hydrosulphurous Acid*). **Formula, H_2SO_2.**

Is produced by the action of metallic zinc on ordinary B.P. sulphurous acid. No gas is given off, and the zinc dissolves quietly, forming a yellow solution. Like sulphurous acid, it possesses bleaching properties, but in a much more intense degree. It is, however, very unstable. Sodium hyposulphite—Na_2SO_2—(*which must not be confused with the so-called hyposulphite of soda, B.P.*) is obtained by the action of zinc on a saturated solution of sodium hydrogen sulphate. It is unstable in the air, and when heated with oxalic acid, evolves hyposulphurous acid as an orange-coloured liquid.

SULPHUROUS ANHYDRIDE. Formula, SO_2. Molecular Weight, 64. Density, *referred to Hydrogen,* **32.**

Sulphurous anhydride is a colourless gas with an exceedingly suffocating odour, and more than twice as heavy as air. Owing to its great solubility in water, it must be collected either over mercury or by displacement. It can be liquefied by drying and passing into a receiver, surrounded by a freezing mixture of ice and salt. The liquid thus obtained can be solidified by the cold produced by its own evaporation *in vacuo.* The gas is formed—

1. Whenever sulphur is burned in the air :—

$$S_2 + 2O_2 = 2SO_2.$$

2. When strong sulphuric acid is heated with most metals, except gold and platinum :—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

3. When strong sulphuric acid is heated with reducing agents, such as sulphur and carbon.

This latter is the process adopted by the B.P., which prepares sulphurous acid by heating sulphuric acid with charcoal, and passing the resulting sulphurous anhydride into water, one gallon of which at 60° will absorb 45 gallons of the gas, and yield a colourless acid, smelling strongly of SO_2, containing 9·2 per cent. by weight of that gas, and having a specific gravity of 1·04.

$$H_2SO_4 + C = SO_2 + CO + H_2O.$$

$$SO_2 + H_2O = H_2SO_3.$$

Sulphurous acid is a powerful deoxidizing agent, owing to its tendency to attract oxygen and form sulphuric acid. It is also a bleacher, but not a permanent one, as the bleaching is not caused, as in the case of chlorine, by oxidation, but simply by a combination of the colouring matter with the SO_2, which can be decomposed and the colour restored by alkalies or oxidation. For example, indigo blue solution when treated with sulphurous acid, becomes colourless, owing to the formation of *white indigo*, but the colour is reproduced by exposure to heated and moist air. Treated with nascent hydrogen, evolved from zinc and hydrochloric acid, sulphurous anhydride is itself reduced to sulphuretted hydrogen :—

$$SO_2 + 3H_2 = H_2S + 2H_2O.$$

This reaction is taken advantage of by the B.P. for its detection in acetic acid. Treated with iodine in the presence of water, it decomposes the latter, forming sulphuric acid and hydriodic acid :—

$$H_2SO_3 + I_2 + H_2O = 2HI + H_2SO_4.$$

The B.P. therefore uses solution of iodine for ascertaining, volumetrically, **the strength of sulphurous acid.**

(*For more complete information, see Author's* **Analytical Chemistry**, *pages 98 and 157.*)

Sulphurous acid forms a class of salts called *sulphites*, which contain the radical SO_3, acting as a dyad.

Alkaline sulphites are prepared by passing SO_2 into a solution of an alkaline carbonate. Calcium hydrogen sulphite is employed as an antiseptic, under the title of "*bisulphite of lime*." Sulphites were formerly used in bleaching, to destroy **the last traces of chlorine, which, if allowed to remain in the fabric,** would not only cause it to rot, but also affect the colours with which it might afterwards be dyed. Hyposulphites now, however, replace sulphites, being at once cheaper and more effective. Both classes of salts are occasionally termed *antichlores*.

Sulphites are not of sufficient pharmaceutical interest to require a detailed description; but a full account of their reactions will be found under Qualitative Analysis, in the analytical part.

HYDROGEN THIOSULPHATE (SYN. *Thiosulphuric Acid, formerly called Hyposulphurous Acid*). **Formula, $H_2S_2O_3$. Molecular Weight, 114.**

The acid, which may be viewed as being derived from sulphuric acid, H_2SO_4, by the displacement of an atom of oxygen by one of sulphur, is very unstable; and although it may be isolated by the action of sulphurous acid on sulphur in a sealed tube, yet it cannot be preserved for any time. It forms a class of salts called **thiosulphates** (formerly hyposulphites), having S_2O_3 as their acidulous radical, acting as a dyad. They are distinguished by evolving sulphurous anhydride and *depositing sulphur* when acted on by hydrochloric or sulphuric acid. This often causes confusion to the young analyst. Suppose

for example, that he has a solution of sodium thiosulphate, and proceeds to test for metals by adding hydrochloric acid. Immediately a white precipitate is thrown down, which he mistakes for silver, mercury, or lead. He adds ammonium hydrate, which does not affect the precipitate, and immediately decides on lead without a confirmatory test. If, therefore, the precipitate in the first group with HCl be white and very fine, always warm, and smell for SO_2 before going further.

SODIUM THIOSULPHATE (SYN. *Hyposulphite of Soda, B.P.*). **Formula, $Na_2S_2O_3.5H_2O$ Molecular Weight, 248.**

Prepared by boiling sodium sulphite with sulphur :—

$$2Na_2SO_3 + S_2 = 2Na_2S_2O_3.$$

Or by adding sulphur to a solution of sodium carbonate, and passing through it a stream of sulphurous anhydride :—

$$Na_2CO_3 + S + SO_2 + 5H_2O = Na_2S_2O_3.5H_2O + CO_2.$$

Commercially it is prepared from the "*soda waste*" and "*gas lime*," both of which contain calcium sulphide, by exposing it to the air so as to convert it into thiosulphate, and making a double decomposition with sodium carbonate, thus :—

$$2CaS_5 + 3O_2 = 2CaS_2O_3 + 3S_3.$$
$$CaS_2O_3 + Na_2CO_3 = Na_2S_2O_3 + CaCO_3.$$

The solution, filtered from the precipitated calcium carbonate, is evaporated and crystallized. The salt forms into large crystals, soluble in water, but not in alcohol. It is fusible by heat, and if melted in a clean flask at 212° F., the mouth being instantly closed with a cork, it will remain fluid; but the moment that the cork is removed, and the surface of the liquid touched with a particle of anything solid, the whole flies into a mass of crystals.

A white precipitate of $Ag_2S_2O_3.H_2O$ (or $Ag_2H_2S_2O_4$), results from the addition of thiosulphate to argentic nitrate, if the latter be kept in excess. By a gradual decomposition this becomes argentic sulphide, Ag_2S, thus :—

$$Ag_2S_2O_3.H_2O = Ag_2S + H_2SO_4.$$

The transformation is rendered visible by the insoluble product being black. If too much sodium thiosulphate be used, the white precipitate of hydrated argentic thiosulphate, at first formed, will be redissolved. It is a curious chemical fact, that the addition of a little argentic chloride to a solution of sodium thiosulphate (itself very bitter), forms the sweetest known liquid, which is, however, extremely poisonous.

Solution of sodium thiosulphate will not keep well, even in a stoppered bottle, as it deposits sulphur, and becomes sodium sulphate, so that the volumetric solution should always be tested before being used. When added to a solution of iodine it decolorizes it, forming sodium iodide and *tetrathionate*, thus :—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

It is therefore used for estimating iodine.

(*See Author's* **Analytical Chemistry**, *page* 152.)

HYDROGEN DITHIONATE (SYN. *Dithionic Acid. Hyposulphuric Acid*). **Formula, $H_2S_2O_6$.**

Is prepared by passing sulphurous anhydride through manganic peroxide

suspended in water, and kept cool, by which means manganous dithionate is formed :—

$$MnO_2 + 2SO_2 = MnS_2O_6.$$

This is then treated with barium hydrate :—

$$MnS_2O_6 + Ba2HO = Mn2HO + BaS_2O_6.$$

Lastly, the barium dithionate is exactly decomposed by an equivalent quantity of dilute sulphuric acid, and the liberated dithionic acid concentrated *in vacuo* till it has a density of 1·347. It is distinguished from sulphuric acid by thus forming a soluble salt with barium.

HYDROGEN TRITHIONATE (SYN. *Trithionic Acid*). **Formula, $H_2S_3O_6$.**

Is liberated from its potassium salt by hydrofluosilicic acid, but gradually splits up into sulphur, sulphurous, and sulphuric acids.

Potassium trithionate, $K_2S_3O_6$, is formed by the action of sulphurous anhydride on potassium thiosulphate :—

$$2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S.$$

HYDROGEN TETRATHIONATE (SYN. *Tetrathionic Acid*). **Formula, $H_2S_4O_6$.**

May be produced by the action of sulphurous anhydride on chlorine disulphide, or isolated from its barium salt. Sodium tetrathionate, $Na_2S_4O_6$, is produced when iodine acts on sodium thiosulphate in the volumetric analysis of iodine and available chlorine by the B P. processes.

(*See Author's* **Analytical Chemistry**, *page* 158.)

HYDROGEN PENTATHIONATE (SYN. *Pentathionic Acid*). **Formula, $H_2S_5O_6$.**

Is a colourless and inodorous acid, decomposable by heat into S, SO_2, SO_3, and H_2S, formed by the action of hydrogen sulphide on aqueous sulphurous acid :—

$$5H_2S + 5H_2SO_3 = H_2S_5O_6 + S_5 + 9H_2O.$$

It is also produced by the action of sulphurous acid on chlorine monosulphide.

SULPHURIC ANHYDRIDE (SYN. *Anhydrous Sulphuric Acid*). **Formula, SO_3. Molecular Weight, 80.**

This is a white crystalline substance, very tenacious, and, when perfectly dry, does not show the slightest acid reaction. Dropped upon water, it hisses in a similar manner to a red hot iron, and combines to produce sulphuric acid. It may be formed by direct combination of sulphurous anhydride and oxygen, both perfectly dry and traversed by a long succession of electric sparks.

$$\begin{array}{ccccc} 2SO_2 & + & O_2 & = & 2SO_3. \\ 4 \text{ vols.} & + & 2 \text{ vols.} & = & 4 \text{ vols. in a state of vapour.} \end{array}$$

More commonly it is produced by heating the German fuming sulphuric acid, or sodium hydro sulphate (which see). A ready method is to take advantage of the superior affinity of phosphoric anhydride for water, by distilling ordinary sulphuric acid with that body, the following reaction occurring :—

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

This process is probably the least troublesome to perform. Sulphuric anhydride forms pyro- or anhydro- sulphates with many metallic sulphates, such as those of sodium, hydrogen, or potassium.

METALLIC SULPHATES.

HYDROGEN SULPHATE (SYNS. **Sulphuric Acid.** *Oil of Vitriol. Vitriol. Hydrated Sulphuric Acid. Hydric Sulphate*). **Formula, H_2SO_4. Molecular Weight, 98.**

Prepared by causing sulphurous anhydride to mix with nitric peroxide and steam in a leaden chamber. The various steps of the process are supposed to be as follows :—

1. The sulphur burning in the air yields sulphurous anhydride :—

$$S_2 + 2O_2 = 2SO_2.$$

2. The sulphurous anhydride and steam yield sulphurous acid :—

$$SO_2 + H_2O = H_2SO_3.$$

3. The sulphurous acid and nitric peroxide yield sulphuric acid and nitric oxide :—

$$2H_2SO_3 + N_2O_4 = 2H_2SO_4 + 2NO.$$

4. The nitric oxide meeting with air carried into the chamber with the current of the various vapours, forms nitric peroxide :—

$$2NO + O_2 = N_2O_4.$$

5. The nitric peroxide meeting with a fresh portion of sulphurous acid, forms more sulphuric acid, and is again reduced to nitric oxide :—

$$2H_2SO_3 + N_2O_4 = 2H_2SO_4 + 2NO.$$

6. The nitric oxide is once more oxidized, as shown in 4 ; and again reduced, as shown in 5 ; and so the action goes on, sulphuric acid being continuously formed as long as any nitric oxide remains in the chamber. In theory, therefore, the portion of nitric oxide first introduced will go on transferring an unlimited amount of oxygen from the air, to change sulphurous into sulphuric acid, so long as the supply of the former is kept up ; but in practice it becomes dissipated, and has to be renewed from time to time.

The sulphuric acid first produced is weak, having a gravity of about 1·5. It is then concentrated in leaden pans at a temperature of 400° F., until it ceases to lose water, when it becomes a definite acid, having the formula $H_2SO_4H_2O$, and containing 70·5 per cent. of real sulphuric acid. At this point it begins to attack lead, and dissolve the sulphate produced, and it is therefore transferred to glass or platinum vessels, in which it is further concentrated until it reaches a gravity of 1·843, when it contains 96·8 per cent. of real H_2SO_4, and is called *oil of vitriol* (*Acidum Sulphuricum*, B.P.).

Characters.—A colourless liquid of oily appearance, intensely acid and corrosive, specific gravity 1·843 (showing 96·8 per cent. H_2SO_4). It evolves much heat on the addition of water, owing to chemical action taking place, and the formation of definite hydrates, such as $H_2SO_4H_2O$ and $H_2SO_2.2H_2O$.

The making of oil of vitriol is practically conducted by burning iron pyrites on a hearth communicating by a flue with the leaden chamber. At the back of this hearth is a pot containing sodium nitrate, which when heated becomes nitrite, and is then acted upon by the sulphurous acid, forming potassium sulphate and liberating nitric oxide :—

$$2KNO_2 + SO_2 = K_2SO_4 + 2NO.$$

The nitric oxide is then carried into the chamber with the excess of sulphurous vapours. The furnace is provided with doors to admit a proper quantity of air and to regulate the draught of the vapours, which on entering the chamber encounter the steam from several jets, pointing in various directions, so as to cause a mixing of all the gases ; and thus the manufacture is kept up night and day,

and the weak acid drawn off as it collects on the floor of the chamber. The commercial acid as thus made frequently contains lead from the chamber and evaporating vessels, arsenic from the iron pyrites, and nitric acid, and has consequently to be purified if desired to answer the B.P. tests.

This is done:

1. By adding a little nitric acid, and so converting the volatile arsenious into arsenic anhydride, which will not distil over at the heat of boiling vitriol:—

$$As_2O_3 + 2HNO_3 = As_2O_5 + N_2O_3 + H_2O.$$

2. To the acid thus treated a little ammonium sulphate is added, which in the presence of nitrous compounds becomes decomposed, forming water, free nitrogen, and sulphuric acid:

$$(NH_4)_2SO_4 + N_2O_3 = 2N_2 + 3H_2O + H_2SO_4.$$

The whole acid is then distilled over in a pure state. This is a common but not the best method, as the subsequent treatment with ammonium sulphate may often reduce the arsenic acid formed in the first step, and once more introduce the danger of contamination by arsenious acid. The best method is to heat the commercial acid with one half per cent. of oxalic acid to a temperature of 230° F., in a thin porcelain basin, until all action ceases. Nitrous compounds are thus entirely removed, and the acid being allowed to cool to 212° F., a little powdered potassium dichromate is stirred in until the whole is coloured yellowish green (indicating excess of chromic acid). The acid so treated being now distilled is found to be free from all impurity.

Plumbic sulphate is detected in sulphuric acid by simply diluting with water, when it becomes milky, owing to a deposit of this substance, which, although soluble in strong, is not so in dilute acid.

Arsenic may be detected by diluting freely with water, and obtaining a yellow precipitate on passing through it sulphuretted hydrogen, while *nitrous compounds* are shown by the dark line of colour produced when a solution of ferrous sulphate is carefully poured upon some strong acid.

When seven fluid ounces of sulphuric acid are diluted with water to 83½ ounces the resulting mixture is the *Acidum Sulphuricum dilutum* of the B.P., which has a specific gravity of 1.094 and contains 11.14 per cent. of anhydrous sulphuric acid.

Sulphuric acid when diluted dissolves zinc, iron, and aluminium, with evolution of hydrogen, but is devoid of action on copper or mercury.

Strong cold acid is practically without action on metals, because there is no water present to dissolve the sulphates formed; but when heated, a portion of the strong acid decomposes, evolves sulphurous anhydride, and produces water, in which the sulphates can dissolve, and it then acts freely.

Gold and platinum entirely resist the action of sulphuric acid.

The strong acid has a great affinity for water, and it is therefore employed for drying gases; on the addition of water to the concentrated acid a very large amount of heat is evolved. Its great attraction for the elements of water causes it to attack and carbonize organic matters, such as sugar, woody, and animal tissues.

If that an ounce of syrup be placed in a long ten ounce precipitating glass, and two ounces of heated sulphuric acid be gradually stirred in, a great cloud of steam will arise, and a quantity of solid charcoal will be liberated, which will rise over the glass, and can be turned out on a plate in lumps.

Tartaric and citric acids, with their salts, are thus attacked when heated with strong sulphuric acid, and an odour of burnt sugar is evolved; but formic and oxalic acids and their salts are not charred, but converted into a mixture

of carbonous oxide and carbonic dioxide, by the following abstraction of water :—

$$H_2C_2O_4 - H_2O = CO + CO_2.$$

Alcohol heated with excess of strong acid is also converted, by the abstraction of water, into ethylene (olefiant) gas (C_2H_4) :—

$$C_2H_5HO - H_2O = C_2H_4.$$

Sulphuric acid forms with bases a class of salts called **sulphates**, in which SO_4 acts as a dyad acidulous radical. It is evident, therefore, that in the presence of a monad base more than one class of salts can be formed, and we have :—

1. The neutral salt, in which the two atoms of hydrogen in the acid have been fully replaced by two atoms of the base (*Ex.* K_2SO_4, Na_2SO_4)
2. The acid or *hydrogen* salt, in which only one atom of the hydrogen has been so affected (*Ex.* $KHSO_4$, $NaHSO_4$).

Sulphates have also a great tendency to unite with each other to form double salts; this is especially the case with the sulphates of the hexad radicals, Fe_2, Al_2, and Cr_2, which unite with the sulphates of potassium, sodium, or ammonium, to form a group of double sulphates, called the *alums*. These alums consist of –

i. The sulphate of the alkali.
ii. That of the hexad metal ; and,
iii. Twenty-four molecules of water.

Thus ammonium aluminium sulphate is :—

$$(NH_4)_2SO_4.Al_23SO_4.24H_2O.$$

Or dividing all by 2 (as done in the B.P.) :—

$$NH_4Al(SO_4)_2.12H_2O.$$

Or we can have ammonium ferric sulphate :—

$$(NH_4)_2SO_4.Fe_23SO_4.24H_2O.$$
$$\text{That is } -NH_4Fe(SO_4)_2.12H_2O.$$

Most sulphates are crystalline and soluble in water, the chief insoluble ones being barium, calcium, and plumbic sulphates.

They are also remarkable for being *isomorphous*, and containing water of crystallization, as seen from the following list :—

$MgSO_4.7H_2O$	$CuSO_4.5H_2O.$
$ZnSO_4.7H_2O.$	$CaSO_4.2H_2O.$
$FeSO_4.7H_2O.$	$Na_2SO_4.10H_2O.$
$MnSO_4.7H_2O.$	The alums, $12H_2O.$

AMMONIUM SULPHATE (Syns. *Sulphate of Ammonia. Diammonic Sulphate*) **Formula, $(NH_4)_2SO_4$. Molecular Weight, 132.**

Prepared by neutralizing the ammoniacal liquors of gas-works with sulphuric acid, or by allowing them to percolate through calcium sulphate, and then evaporating and crystallizing. It is used as a source of other ammonium salts, and also as an ingredient of "*top-dressing*," and similar artificial manures. It may be purified by crystallization or by sublimation, but cannot be sublimed alone, and is readily soluble in water. **Ammonium hydrogen sulphate** may be formed by the addition of sulphuric acid to the other sulphate, and is of no importance. Unlike the other sulphate, it is soluble in alcohol.

SODIUM SULPHATE (SYNS. *Disodic Sulphate. Sodæ Sulphas. Glauber Salt. Sulphate of Soda*). **Formula, Na_2SO_4. Molecular Weight, 142.**

It is found in nature in combination with calcium sulphate as *Glauberite*, and also in other forms. It is produced most extensively by the action of sulphuric acid upon sodium chloride in the manufacture of sodium carbonate, and is sold as *salt cake* in a fused and anhydrous condition.

To prepare the B P. crystals, the salt cake is dissolved in water, neutralized, if necessary, by sodium carbonate, and crystallized. It is described in the B P. as being in transparent oblique prisms; has a salt and bitter taste; effloresces on exposure to the air; soluble in water, insoluble in spirit. Exposed to heat in a porcelain crucible, it loses 55·9 per cent. of water of crystallization.

(*For analysis and impurities see Author's* **Analytical Chemistry**, *page* 99.)

This substance exhibits pre-eminently the curious property of *super saturation*, that is to say, a boiling saturated solution may be kept in a corked flask without solidifying on cooling But on opening the flask and giving it a slight shake, the whole flies into a solid mass of crystals, with a sudden evolution of heat. Much of the sodium sulphate of commerce is obtained from the residue in the retort after the preparation of chlorine in the manufacture of *chlorinated lime*. This residue is mixed with calcium hydrate, by which the manganous sulphate is transformed into manganous hydrate, which, together with the calcium sulphate formed, may be separated by filtration. If insufficient calcium hydrate be used, a little manganous sulphate remains in solution, and will give a precipitate on the addition of potassium hydrate, turning brown on pouring in a little chlorine water.

SODIUM HYDROGEN SULPHATE (SYNS. *Acid Sodium Sulphate. Monosodic Sulphate. Bisulphate of Soda*). **Formula, $NaHSO_4$. Molecular Weight, 120.**

Arises from the action of sulphuric acid on sodium nitrate in the preparation of nitric acid, and much resembles potassium hydrogen-sulphate in its properties, but is very deliquescent, and consequently has a very limited application. By bringing the crystals in contact with alcohol and water (or moist air) they are decomposed, sulphuric acid being set free. Thus it may be said that the salt itself is not deliquescent, but the sulphuric acid always adhering to the crystals attracts moisture, which then causes the decomposition of the salt. This sulphate forms a crystallizable combination with sodium sulphate.

POTASSIUM SULPHATE (SYNS. *Dipotassic Sulphate. Potassæ Sulphas. Sulphate of Potash. Sal Polychrest*). **Formula, K_2SO_4. Molecular Weight, 174.**

Produced during the process for preparing iodine from kelp, as the first crop of crystals obtained after lixiviation.

It is also prepared by neutralizing the potassium hydro-sulphate with potassium carbonate.—

$$2KHSO_4 + K_2CO_3 = 2K_2SO_4 + CO_2 + H_2O.$$

In nature it is found as a crust on the lava of volcanoes, especially that of Mount Vesuvius. The B P. describes it as being in colourless, hard, six sided prisms terminated by six sided pyramids, decrepitates strongly when heated; sparingly soluble in water; insoluble in alcohol.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 99.)

It is used in Pharmacy as a triturant, owing to its hard and gritty character tending to divide powders which would otherwise aggregate under the pestle. It contains no water of crystallization; and at ordinary temperatures water will not dissolve more than $\frac{1}{16}$ of its weight. It has a saline, unpleasant, and bitter taste. Phosphoric and nitric acids combine with it to form definite crystallizable salts, no decomposition whatever occurring.

POTASSIUM HYDROGEN SULPHATE (Syns. *Acid Sulphate of Potassium. Monopotassic Sulphate. Bisulphate of Potash*). **Formula, $KHSO_4$. Molecular Weight, 136.**

Is a bye-product in the manufacture of acids, notably of nitric acid from potassium nitrate. It is generally found, as sold for analysis, in white crystalline masses, evidently broken from thick cakes, and is used in the analysis of refractory minerals, such as chrome ores, owing to its power, when fused, of liberating sulphuric anhydride. When first heated, it fuses and loses water, forming potassium anhydro-sulphate :—

$$2KHSO_4 = K_2SO_4.SO_3 + H_2O.$$

At an increased temperature it liberates sulphuric anhydride, which passes off in white fumes :—

$$K_2SO_4.SO_3 = K_2SO_4 + SO_3.$$

A solution of potassium hydro-sulphate (which is very soluble in water) is not stable, potassium sulphate depositing after some time, unless it be very dilute.

On vegetable colouring principles its action resembles that of an acid.

ARGENTIC SULPHATE (Syn. *Sulphate of Silver*). **Formula, Ag_2SO_4. Molecular Weight, 312.**

Prepared by dissolving silver in strong boiling sulphuric acid. It is in brilliant colourless crystals soluble in strong sulphuric acid, and in 200 parts of cold water. It is employed for the purpose of removing chlorides from any solution in which it is desired to estimate the nitrogen present as nitrates or nitrites by Crum-Brown's method.

CALCIUM SULPHATE (Syns. *Gypsum. Alabaster. Sulphate of Lime. Plaster of Paris. Anhydrite*). **Formula, $CaSO_4$. Molecular Weight, 136.**

Is found native as *gypsum*, $CaSO_4.2H_2O$, which when exposed to a high temperature (220° to 250° F.) loses part of its water, and becomes the well-known *plaster of Paris*. On mixing the plaster with water, to the consistence of cream, it recombines, and *sets* into a hard mass of crystalline sulphate.

Calcium sulphate in the crystalline state is very slightly soluble in water, one part only dissolving in 350 of water; and raising the temperature of the water does not perceptibly increase its solubility. Its solution is used to detect oxalic acid in tartaric or citric acids. The small amount of calcium present is precipitated only by the oxalic acid; the calcium tartrate and citrate being dissolved by the large amount of water in proportion.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 99.)

Solution of sulphate of lime, B.P., is ordered to be made with more than four times as much calcium sulphate as can be dissolved.

STRONTIUM and BARIUM SULPHATES. Formulæ, $SrSO_4$ *and* $BaSO_4$. Molecular Weights, 183·5 *and* 233.

Found native; the former as *cœlestine*, and the latter as *heavy spar*. Both are produced as white precipitates when sulphuric acid is added to a soluble salt of the respective metals. They are absolutely insoluble in everything; but for the purpose of detecting the sulphuric acid contained in them, they may be decomposed by fusion with potassium or sodium carbonate.

MAGNESIUM SULPHATE (SYNS. *Magnesiæ Sulphas. Epsom Salts. Sulphate of Magnesia*). **Formula, $MgSO_4.7H_2O$. Molecular Weight, 246.**

Is prepared by dissolving magnesium carbonate in sulphuric acid :—

$$MgCO_3 + H_2SO_4 = MgSO_4 + CO_2 + H_2O.$$

The carbonate employed is usually the mineral termed *dolomite*, which contains both magnesium and calcium carbonates. By the action of the acid, calcium and magnesium sulphates are produced, and the mass having been digested with water, the latter is dissolved, leaving the former insoluble.

Magnesite, which is also a native form of magnesium carbonate, being nearly pure, may be simply dissolved in sulphuric acid, and the solution evaporated to the crystallizing point. Occasionally magnesium sulphate is produced from *dolomite* by calcination, moistening the oxides formed with water, and dissolving out the calcium hydrate by hydrochloric acid; which, if added in small quantities, will take up all the calcium hydrate before affecting the magnesium hydrate. The insoluble product is treated with sulphuric acid, by which it is dissolved; or with ferrous sulphate, which transforms it into magnesium sulphate and insoluble ferrous hydrate, quickly converted by exposure to the air into ferric hydrate. Magnesium sulphate is also found native as *Epsomite*, and exists in many mineral waters, notably those of Seidlitz in Bohemia, and of Epsom in Surrey, from which it takes its common name of Epsom salts. It is thus described by the B.P. :—

Characters and Tests.—In minute colourless and transparent rhombic prisms, possessing a bitter taste, and freely soluble in water.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 99.)

Its great similarity to zinc sulphate renders it desirable that all chemists should know some ready test to apply in case of doubt. The reagent which will best serve the purpose is potassium ferrocyanide, which, when added to a solution of the suspected salt made fairly dilute, gives no precipitate with magnesium sulphate, but forms a white jelly with zinc sulphate.

Water will dissolve its own weight of the crystalline salt at ordinary temperatures; three parts of boiling water will take up four parts, while proof spirit will only dissolve $\frac{1}{8}$ per cent., and in absolute alcohol it is insoluble. When crystallized magnesium sulphate is heated, it loses six molecules of its water of crystallization; but the seventh remains even at high temperatures, and is therefore considered as *water of constitution*. At a red heat this water passes off, and leaves a fused mass of $MgSO_4$, which is not decomposed except at very high temperatures, and then only slightly. Solution of magnesium sulphate exhibits the property of supersaturation. When mixed with ammonium hydrate, and ammonium chloride added until the precipitate is redissolved, it is used as a precipitant of phosphoric acid, which it throws down as magnesium ammonium phosphate. Magnesium sulphate containing iron may be purified by ignition and subsequent solution, filtration, and crystallization. The thin sharp needles in which it crystallizes have caused the efflorescence of the salt sometimes occurring on minerals to be termed *hair salt*.

ZINC SULPHATE (SYNS. *Zinci Sulphas. Sulphate of Zinc. White Vitriol*). **Formula, $ZnSO_4.7H_2O$. Molecular Weight, 287.**

Prepared by dissolving metallic zinc in dilute sulphuric acid:—

$$Zn_2 + 2H_2SO_4 = 2ZnSO_4 + 2H_2.$$

In practice the solution thus obtained is filtered into a bottle, and solution of chlorine added until the fluid acquires a permanent odour of chlorine. The whole is then shaken up with zinc carbonate until a brown precipitate appears, and the solution is separated by filtration, evaporated till a pellicle forms on the surface, and set aside to crystallize.

(*For analysis and impurities, see Author's* **Analytical Chemistry,** *page* 99.)

The reason for the treatment with chlorine water and zinc carbonate, is to ensure freedom from iron and lead, with which metallic zinc is usually contaminated. (*See* **Zinc Chloride.**)

Zinc sulphate is described as being:—

In colourless, transparent, prismatic crystals, with a strong metallic styptic taste.

100 parts of water at the ordinary temperature will dissolve about 150 parts of the crystallized salt, and at boiling heat about 650 parts. It is insoluble in alcohol, and very slightly soluble in spirit. Like magnesium sulphate, it contains one molecule of water of constitution, which is only driven off at a temperature of about 500° F.; but if the heat be increased to redness, pure zinc oxide only remains.

The emetic properties of the zinc sulphate form the chief safeguard when this salt has been mistaken for the magnesium sulphate.

CUPRIC SULPHATE (SYNS. *Cupri Sulphas. Sulphate of Copper. Blue Vitriol. Blue Copperas. Blue Stone*). **Formula, $CuSO_4.5H_2O$. Molecular Weight, 249·5.**

Prepared by dissolving copper with the aid of heat in strong sulphuric acid.

$$Cu_2 + 4H_2SO_4 = 2CuSO_4 + 2SO_2 + 4H_2O.$$

The objection to this process is, that sulphurous anhydride and some copper are wasted in consequence of a secondary action, resulting in the formation of cupric sulphide:—

$$Cu_2 + 2SO_2 = CuSO_4 + CuS.$$

Commercially, cupric sulphate is produced from copper pyrites, which is a double sulphide of copper and iron ($Cu_2S.Fe_2S_3$). On exposing this mineral to the air, and gently roasting, with free access of air, it is decomposed into cupric sulphate and cupric and ferric oxide:—

$$Cu_2S.Fe_2S_3 + 7O_2 = CuSO_4 + CuO + Fe_2O_3 + 3SO_2.$$

No doubt both cupric and ferrous sulphates are first produced, and afterwards the latter is destroyed by the heat. The reduction to ferric oxide is, however, rarely complete, and the crude cupric sulphate is almost invariably contaminated with ferrous sulphate. Cupric sulphate is also a bye-product in silver refining. (*See* **Silver.**) The commercial salt should always be tested for iron with chlorine water and ammonium hydrate. The former raises the ferrous sulphate to ferric sulphate, and the latter causes a brown precipitate of ferric hydrate which remains floating in the deep-blue solution, and can be seen by holding the tube between the eye and the light. To obtain the absolutely pure salt, commercial sulphate should be dissolved in warm water, and a few drops of nitric acid added, which will convert the ferrous into ferric sulphate.

A little cupric oxide is added, which will precipitate the iron, and the whole is finally to be filtered and crystallized.

Cupric sulphate is occasionally formed from the black scales with which copper becomes coated when heated in the air. These are cupric oxide, and yield a very pure salt when dissolved in dilute sulphuric acid:—

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Ordinary cupric sulphate is a blue crystalline salt, in oblique prisms, soluble in water, forming a pale blue solution which strongly reddens litmus.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 100.)

At 60° F. water dissolves 40 per cent. of its weight of cupric sulphate, whilst at 212° F. it dissolves about twice its own weight. When heated to 400° F. cupric sulphate loses its water of crystallization, and becomes a white powder. On contact with moisture this powder turns blue, and is therefore an excellent test for the presence of water in fluids such as ether, absolute alcohol, or chloroform. It is called *cupri sulphas exsiccata* in the B.P. Cupric sulphate is not readily decomposed by heating above 400° F.

AMMONIUM CUPRIC SULPHATE (SYN. *Double Sulphate of Ammonia and Copper*). **Formula, $Cu(NH_4)_2 2SO_4 . 6H_2O$.**

Is produced in large blue crystals, by mixing solutions of the two sulphates, and crystallizing. It is soluble in water, yields the characteristic blue precipitate of cupric salts with ammonium hydrate, and does not spontaneously evolve fumes of ammonia. By these points it is distinguished from the following compound, with which it must not be confused.

TETR-AMMONIO CUPRIC SULPHATE (SYNS. *Ammonio Sulphate of Copper, Diammonium Cupro-diamine Sulphate*). **Formula, $Cu(NH_3)_4 SO_4 . H_2O$.**

Is produced in solution by adding ammonium hydrate drop by drop to a solution of cupric sulphate, until the precipitate first formed is nearly but not quite redissolved, and filtering. This solution is used (under the name of ammonio sulphate of copper) to detect the presence of arsenious acid, with which it forms cupric arsenite (*Scheele's green*). When it is mixed with strong alcohol it deposits the salt in blue crystals, which may be dried by pressure between folds of blotting paper. When heated, the crystals become decomposed, first forming cupr ammonium sulphate, $CuNH_3SO_4$; and finally, as the heat approaches 500° F., that compound is in turn reduced to cupric sulphate.

To understand the constitution of tetr ammonio cupric sulphate it is necessary to observe that the full atomicity of nitrogen being pentad (N^v), that of ammonia (NH_3) will be dyad, because there are two atomicities of the nitrogen left unsaturated. But the dyad NH_3 can combine with other molecules of itself indefinitely, always preserving its dyad atomicity, thus:—

$$\begin{array}{c} -N- \\ ||| \\ H_3 \\ NH_3 \end{array} \qquad \begin{array}{c} -N-N- \\ |||\ \ ||| \\ H_3\ \ H_3 \\ 2NH_3 \end{array} \qquad \begin{array}{c} -N-N-N- \\ |||\ \ |||\ \ ||| \\ H_3\ \ H_3\ \ H_3 \\ 3NH_3 \end{array}$$

The atom of copper, itself a dyad, can also combine with one molecule of ammonia, and produce a basylous radical, **cuprammonium**, which will still retain the dyad atomicity, thus:—

$$\begin{array}{c} -N-Cu- \\ ||| \\ H_3 \end{array} \rightarrow \left(N \begin{cases} H \\ H \\ H \\ Cu \end{cases} \right)$$

By multiplying the molecules of ammonia, we could produce another radical, **cuprodiammonium**, still a dyad.

$$\begin{array}{c} -N-N-Cu- \\ \vdots\quad\vdots \\ H_3\ \ H_3 \end{array} = \left(\begin{array}{l} N\left\{H_3\right. \\ \quad Cu \\ N\left\{H_3\right. \end{array}\right)$$

Advancing two steps further, we have.—

$$\begin{array}{c} -N-N-N-N-Cu- \\ \vdots\quad\vdots\quad\vdots\quad\vdots \\ H_3\ \ H_3\ \ H_3\ \ H_3 \end{array} = \left(\begin{array}{l} N\left\{H_3\right. \\ \quad Cu \\ N\left\{H_3\right. \\ N\left\{H_3\right. \\ N\left\{H_3\right. \end{array}\right)$$

of which radical the compound under consideration is the sulphate, thus,—

$$\left(\begin{array}{c}(NH_3)_4 \\ Cu\end{array}\right) SO_4 + H_2O.$$

Similar **metallammoniums** will be found described under **Mercuric Chloride** and **Argentic Nitrate.**

MERCUROUS SULPHATE (SYN. *Sub-Sulphate of Mercury*). **Formula, Hg_2SO_4. Molecular Weight, 496.**

Produced during the manufacture of mercurous chloride, when mercuric sulphate is rubbed and heated with metallic mercury.

$$Hg_2 + 2HgSO_4 = 2Hg_2SO_4.$$

It is a white powder, very slightly soluble either in cold or in warm water.

MERCURIC SULPHATE (SYNS. *Hydrargyri Sulphas. Persulphate of Mercury*). **Formula, $HgSO_4$. Molecular Weight, 296.**

Prepared by heating mercury in strong sulphuric acid:—

$$Hg_2 + 4H_2SO_4 = 2HgSO_4 + 4H_2O + 2SO_2.$$

Characters.—A white crystalline heavy powder, rendered yellow by affusion of water. Entirely volatilized by heat.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 100.)

The first character is due to the formation of *Turpeth mineral* (mercuric oxysulphate, $HgSO_4.2HgO$).

The volatilization test shows its freedom from salts of lead and tin. Mercuric oxysulphate is also formed on boiling mercuric sulphate with water, when it separates as a yellow powder only slightly soluble in water. Mercuric sulphate has an extremely unpleasant, acrid, metallic, and saline taste. It melts at a strong red-heat, forming a dark-coloured liquid, which volatilizes with but slight dissociation, and forms a white sublimate. The yellow *Turpeth mineral* becomes grey by atmospheric action.

ALUMINIUM AMMONIUM SULPHATE (SYNS. *Alumen, B.P. Alum, P.L. Ammonia Alum*). **Formula, $NH_4Al(SO_4)_2.12H_2O$. Molecular Weight, 453·5.**

The manufacture of alum was commenced in England as early as the year 1680. The great centres of manufacture are Hurlet, near Glasgow, and

Whitby, in Yorkshire; at both of which places it is prepared from *alum shale*, a mineral having, roughly speaking, the following composition:—

Aluminium Silicate (Clay)	63
Ferrous Disulphide (Pyrites)	15
Carbon (Coal)	13
Calcium, Magnesium, Manganese, etc.	9
	100

When this mineral is exposed to the action of air and moisture, the pyrites is converted into ferrous sulphate, with liberation of sulphuric acid:—

$$2FeS_2 + 2H_2O + 7O_2 = 2FeSO_4 + 2H_2SO_4.$$

Immediately on its liberation the sulphuric acid attacks the clay, forming aluminium sulphate. The mineral is cut from the seams, and laid in immense heaps, exposed to the air, often for as long as fifteen years. During this time the change above mentioned sets in, and the mineral splits, disintegrates, and becomes converted into a silky looking mass of aluminium sulphate studded with green crystals of ferrous sulphate. The changed material is then made into fresh heaps, laid on brushwood, and set on fire, when the carbonaceous matter burns away, and the ferrous sulphate is partly decomposed; this action taking about eight months. The mass is digested in water and the solutions having been clarified by subsidation, are concentrated and mixed with ammonium sulphate, when impure alum immediately crystallizes out. It is purified by three successive recrystallizations, the last one being performed in a tub, which is taken to pieces by removing the hoops and the alum recovered as a magnificent crystalline mass.

Alum is also occasionally produced by a quick process from shale. This is roasted and then heated with sulphuric acid. When the decomposition is tolerably complete, ammonium hydrate is added, until it is found that the solution will crystallize on cooling, at which point it is allowed to do so. The crystals, however, thus formed are not large; and as in any case the product would require recrystallization, the liquid is frequently stirred, so that *alum flour* deposits, which can be more readily redissolved than crystals.

The *ammonium alum* is the only one mentioned by the B.P., but potassium alum is frequently manufactured by the substitution of potassium sulphate for the ammonium sulphate of the last case. Its formula is $KAl(SO_4)_2.12H_2O$.

When boiled with ammonium hydrate, solution of alum yields a precipitate of aluminium hydrate, but it is not affected by boiling with excess of potassium or sodium hydrate. The ammonium alum is distinguished by giving off the smell of ammonia gas when boiled with either of the two last-mentioned hydrates. By heating to a temperature not exceeding 400° F., alum gives up its ammonium sulphate and water of crystallization, becoming *burnt alum* (*alumen exsiccatum*, B.P.), which is a white mass, hygroscopic, and very nearly insoluble in water. When heated to redness, ammonium alum is entirely decomposed, leaving a residue of aluminium oxide. Alum is described in the B.P. as being in colourless transparent crystalline masses, exhibiting the faces of the regular octahedron, and having an acid sweetish astringent taste.

(*For anaylsis, see Author's* **Analytical Chemistry**, *page* 100.)

ALUMINIUM SULPHATE (SYNS. *Patent Alum. Alum Cake. Sulphate of Alumina*). **Formula, $Al_2 3SO_4.9H_2O$. Molecular Weight, 505.**

Is prepared from shale and other aluminous silicates, by a process resembling that for the manufacture of alum. No ammonium sulphate, however, or

other source of ammonium is added. This salt is at the present time used for many of the purposes for which alum was at one time in demand. It occurs native as *feather alum*, and is insoluble in alcohol, but soluble in twice its weight of water.

MANGANOUS SULPHATE. **Formula, $MnSO_4 7H_2O$. Molecular Weight, 277.**

Is formed when manganic peroxide is heated with sulphuric acid, oxygen being evolved. It crystallizes in pale rose-coloured crystals. The temperature at which it crystallizes affects the amount of water of crystallization.

FERROUS SULPHATE (SYNS. *Ferri Sulphas. Copperas. Green Vitriol. Sulphate of Iron. Protosulphate of Iron*). **Formula, $FeSO_4 7H_2O$. Molecular Weight, 278.**

Is prepared by dissolving iron in *diluted* sulphuric acid by the aid of a gentle heat, and crystallizing.

$$Fe_2 + 2H_2SO_4 = 2FeSO_4 + 2H_2.$$

When iron is heated with strong sulphuric acid, ferrous sulphate and sulphurous anhydride result, but this is too wasteful a process to be of practical value :—

$$Fe_2 + 4H_2SO_4 = 2FeSO_4 + 2SO_2 + 4H_2O.$$

The solution of ferric oxide, or rust, in diluted sulphuric acid, and addition of scraps of iron, was formerly used for the preparation of ferrous sulphate, but is now seldom adopted, because of the liability of the ferric oxide to contain earthy matters, either as an adulteration or as an accidental contamination.

Ferrous sulphate is produced commercially by the spontaneous oxidation of white iron pyrites in contact with the air; and is crystallized out from the liquor in which the disintegrated mineral has been lixiviated. The B.P. thus describes it :—

In oblique rhombic prisms, of a pale greenish-blue colour and styptic taste; insoluble in rectified spirit, soluble in water.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 100.)

Ferrous sulphate being insoluble in alcohol, it follows that if a strong watery solution be poured into rectified spirit, the salt will form a precipitate consisting of very minute crystals of $FeSO_4.7H_2O$. This preparation is called *ferri sulphas granulata*, B.P. and is in small granular crystals of a pale greenish blue colour, well adapted for dispensing purposes. In other respects it corresponds to the characters and tests for ferrous sulphate.

This form of ferrous sulphate is much less readily oxidized by the action of the air than the ordinary crystals, and in consequence is an admirable pharmaceutical preparation.

When heated to 212° F., ferrous sulphate gives up its water, and continues to do so as the heat is raised. At 400° F. it becomes a white mass of $FeSO_4 H_2O$, called *ferri sulphas exsiccata*. If heated beyond 400° it parts with all its water, and immediately begins to decompose, evolving sulphurous and sulphuric anhydrides, and leaving ferric oxide :—

$$2FeSO_4 = Fe_2O_3 + SO_2 + SO_3.$$

When the ordinary sulphate is exposed to the air, it becomes covered with a rusty crust of ferric oxysulphate, and a similar substance is also deposited from solutions exposed to atmospheric influence.

The formula of this crust is :—

$$Fe_23SO_4\,5Fe_2O_3 \text{ ; or more simply, } (Fe_4O_3)SO_4.$$

It is from this crust that the fuming brown sulphuric acid, known as *Nordhausen acid*, is prepared. The sulphate is exposed to the air till thoroughly rusted, and then distilled in earthenware retorts, when the acid passes over. This acid is a solution of sulphuric anhydride in sulphuric acid, thus —$H_2SO_4.SO_3$.

On account of its great affinity for oxygen, ferrous sulphate is much used as a reducing agent in analysis. For instance, if an excess of it be mixed with solution of auric chloride, metallic gold is precipitated. It is sometimes used for the estimation of permanganates and chromates or dichromates, in consequence of the great tendency of the iron to assume the ferric state. A large amount is employed in dyeing, and in the preparation of prussian blue and ink.

FERRIC SULPHATE (SYNS. *Ferri Persulphas. Persulphate of Iron*). **Formula, Fe_23SO_4. Molecular Weight, 400.**

Is a yellowish-white powder, but rarely used in the solid state in pharmacy. It is employed in the form of a strong solution, called *liquor ferri persulphatis*, which is prepared by dissolving ferrous sulphate in diluted sulphuric acid, and warming with a little nitric acid, until the black colour at first produced changes to reddish-brown. The nitric acid becomes reduced to nitric oxide, and liberates nascent oxygen, which immediately combines with the hydrogen of the sulphuric acid, allowing the excess of SO_4 to combine with the ferrous sulphate and form the ferric salt :—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_23SO_4 + 2NO + 4H_2O.$$

The black colour produced on first adding the nitric acid is caused by the production of nitric oxide and its union with the ferrous sulphate. (*See* **Nitric Oxide.**) The compound is, however, immediately decomposed by the heat employed.

Characters.—A dense solution of dark red colour, inodorous, and very astringent, miscible in all proportions with alcohol and water :—specific gravity, 1·441.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 101.)

When the solution is evaporated to dryness a yellowish red residue is left, which becomes lighter in colour if heated, and is afterwards much less readily soluble in water than before. If the temperature be raised very high, sulphuric anhydride is driven off, and it has been proposed to utilize this property for the preparation of that body.

When solution of ferric sulphate is digested with ferric hydrate, a basic sulphate is formed, which appears on evaporation as a gummy uncrystallizable mass. This is only one of many such basic ferric sulphates which have been discovered.

FERRIC POTASSIUM SULPHATE and FERRIC AMMONIUM SULPHATE (SYNS. *Iron Alum. Ammonio-Iron Alum. Potassio-Iron Alum*). **Formulæ, $NH_4Fe(SO_4)_2.12H_2O$ *and* $KFe(SO_4)_2.12H_2O$.**

These alums (much used by dyers) crystallize in beautiful crystals, isomorphous with those of ordinary alum. The potassium salt has an amethyst tint, while the ammonio-ferric sulphate is always colourless, like ammonio-aluminium sulphate.

Iron Alum is prepared by heating a mixture of two molecules of ferrous sulphate, one molecule of potassium or ammonium sulphate, and one molecule of sulphuric acid, with sufficient nitric acid to change the iron to the ferric state, and then crystallizing. It is liable to become rusty outside, owing to the formation of basic sulphate; and consequently the true salt is but too often imitated, and thus sold as *roche alum*, by simply crystallizing common alum with a little red ochre, or other earth containing ferric oxide. Iron alum is employed when a perfectly neutral solution of a ferric salt is required in analysis or by dyers.

The ammonio-iron alum has been introduced as a remedial agent.

PLUMBIC SULPHATE (SYN. *Sulphate of Lead*). **Formula, $PbSO_4$. Molecular Weight, 303.**

Produced as a white precipitate on treating a soluble salt of lead (such as plumbic acetate) with sulphuric acid:—

$$Pb2C_2H_3O_2 + H_2SO_4 = PbSO_4 + 2HC_2H_3O_2.$$

It is nearly insoluble in water, and absolutely so in spirit. It is soluble to some extent in strong sulphuric acid, from which it is reprecipitated by dilution with water. It is attacked slightly by hydrochloric and nitric acids, and entirely dissolved by sodium or potassium hydrates, and by ammonium acetate. Plumbic and barium sulphates may be easily separated by digestion in a solution of the last-named reagent, the barium remaining undissolved.

BISMUTHOUS SULPHATE (SYN. *Sulphate of Bismuth*). **Formula, Bi_23SO_4. Molecular Weight, 708.**

Prepared by the solution of the metal in strong hot sulphuric acid:—

$$Bi_2 + 6H_2SO_4 = Bi_23SO_4 + 3SO_2 + 6H_2O.$$

By diluting the solution, a reaction somewhat like the following occurs:—

$$\underset{\text{(Bismuthous Sulphate.)}}{2Bi_23SO_4} + 2H_2O = \underset{\text{(Bismuthyl Sulphate.)}}{(BiO)_2SO_4} + \underset{\text{(Hydro-Bismuthous Sulphate.)}}{Bi_2H_4(SO_4)_5}.$$

CHROMIC SULPHATE (SYNS. *Sulphate of Chromium. Sulphate of Sesquioxide of Chromium*). **Formula, Cr_23SO_4.**

Exists in two modifications, viz., violet and green: the former results from the digestion of chromic hydrate dried at 212° F. with strong sulphuric acid for a month. The latter from the solution of moist chromic hydrate in sulphuric acid at a temperature of about 130° F. Either of these modifications yields, when heated to 400° F. with excess of sulphuric acid, a red chromic sulphate, perfectly insoluble in water.

CHROMIC POTASSIUM SULPHATE (SYN. *Chrome Alum*). **Formula, $KCr(SO_4)_2 12H_2O$.**

May be prepared by gently heating solution of potassium dichromate with an exact quantity of sulphuric acid, dropping in a little spirit till the whole turns green, and crystallizing. The spirit is simply used to hasten the action. The equation has been already given. (*See page* 80.)

It crystallizes in regular octahedrons of a magnificent deep claret colour, and yields a dark-green solution, and is much used by dyers. An ammonium

chrome alum is also known, $NH_4Cr(SO_4)_2 12H_2O$, which may be decomposed by heat, and even by prolonged boiling.

HYDROGEN PYROSULPHATE (SYNS. *Disulphuric Acid. Anhydro Sulphuric Acid. Nordhausen Sulphuric Acid*). **Formula, $H_2S_2O_7$; or $H_2SO_4.SO_3$.**

May be prepared in the crystalline state by adding a molecular weight of sulphuric anhydride to a molecular weight of sulphuric acid. In practice it is made by distilling rusty crystals of ferrous sulphate. As found in commerce it is a brown fuming liquid which becomes solid at 32° Fah., and has a specific gravity of 1·9. **When distilled at a gentle heat it yields sulphuric anhydride,** and leaves sulphuric acid in the retort. It is used by dyers for dissolving indigo and anthraquinone. It forms a small class of salts called pyrosulphates or anhydrosulphates. The potassium salt is $K_2S_2O_7$ or $K_2SO_4SO_3$, and is produced by gently heating potassium hydrogen sulphate.

COMPOUNDS OF SULPHUR WITH THE HALOGENS.

SULPHUR MONOCHLORIDE. Formula, S_2Cl_2 (or 2SCl).

Is a mobile orange-yellow liquid, fuming in the air and having a peculiar odour, which is prepared by distilling sulphur at a gentle heat in a retort kept filled with **dry chlorine, and also by distilling sulphur with mercuric or stannic** chlorides. It has a specific gravity of 1·687, and boils at 277° Fah. It is an excellent solvent for sulphur, and is itself miscible with carbon disulphide. The preparation known in pharmacy as **hypochloride of sulphur,** and used in skin diseases, is simply the monochloride thus saturated with sulphur. A solution of it in benzol saturated with sulphur is used for vulcanizing india rubber. In contact with water, alcohol, or ether, it is at once decomposed, the action with the first-named being :—

$$2S_2Cl_2 + 3H_2O = S_3 + H_2S_2O_3 + 4HCl.$$

By cooling in a freezing mixture of ice and salt, and passing chlorine to saturation, it is transformed into **sulphur dichloride,** SCl_2, which is a deep red liquid; and by increasing the cold to −4° Fah. more chlorine can be absorbed, and a **tetrachloride** produced, having the formula SCl_4. This latter product, when acted upon by sulphuric anhydride, behaves thus :—

$$SO_3 + SCl_4 = SOCl_2 + Cl_2 + SO_2.$$

THIONYL CHLORIDE (SYNS. *Sulphurous Chloride. Oxychloride of Sulphur*). **Formula, $SOCl_2$.**

Is a colourless and highly refractive liquid, boiling at 180° Fah., which is prepared—

(1) By the action of sulphurous anhydride on phosphoric chloride :—

$$PCl_5 + SO_2 = SOCl_2 + POCl_3.$$

(2) By the action of phosphorous oxychloride on calcium sulphite :—

$$2POCl_3 + 3CaSO_3 = 3SOCl_2 + Ca_3 2PO_4.$$

On touching water, it forms hydrochloric and sulphurous acids; and on mixing **with an alcohol, it forms the corresponding haloid ether :—**

$$2C_2H_5HO + SOCl_2 = 2C_2H_5Cl + H_2SO_3.$$

SULPHURYL CHLORIDE (SYNS. *Sulphuric Oxychloride. Chlorosulphuric Acid*). **Formula, SO_2Cl_2.**

Results from the prolonged exposure of sulphurous anhydride and chlorine to direct sunlight; and may also be prepared by distilling sulphuric acid with phosphoric chloride.

$$2PCl_5 + H_2SO_4 = SO_2Cl_2 + 2POCl_3 + 2HCl.$$

It is a fuming liquid, boiling at 170° Fah., and having a specific gravity of 1·66. It behaves like thionyl chloride with alcohol, except that it forms sulphuric instead of sulphurous acid, which, in the case of alcohol, attacks the excess of that body and forms ethyl sulphuric acid.

By the action of water molecule to molecule it yields **sulphuric chlorhydrate,** $HClSO_3$, or *chlorohydrosulphurous acid,* thus:—

$$SO_2Cl_2 + H_2O = HClSO_3 + HCl.$$

BROMINE MONOCHLORIDE.

Results from the solution of sulphur in bromine, but has not been obtained in a state of purity.

IODINE MONOSULPHIDE (SYN. *Sulphuris Iodidum*). **Probable formula, S_2I_2**

Prepared by heating iodine with sulphur.

The B.P. directs the iodine and sulphur (in the proportion of 4 to 1 by weight) to be rubbed together in a mortar until they are thoroughly mixed. Put the mixture into a flask, close the orifice loosely and apply a gentle heat, so that the colour of the mass shall become gradually darkened. When the colour has become uniformly dark throughout, increase the heat so as to produce liquefaction. Then incline the flask in different directions, in order to return into the liquid any portion of the iodine which may have been condensed on the inner surface of the vessel. Lastly, withdraw the heat, and when the liquid has congealed, remove the mass by breaking the flask, reduce it to pieces, and keep these in a well-stoppered bottle.

Characters and Tests.—A greyish-black solid substance, with a radiated crystalline appearance. It resembles iodine in smell, and in the property of staining the cuticle when applied to it. Soluble in sixty parts of glycerin, and insoluble in water, but when boiled in water is decomposed. If 100 grains be thoroughly boiled with water, the iodine will pass off in vapour, and about 20 grains of sulphur will remain (correct proportion of iodine and absence of impurities).

CHAPTER VIII.

CARBON.

CARBON. Symbol, C. Atomic Weight, 12.

This element is found free in nature, as well as combined in many minerals. In union with oxygen as carbonic anhydride it exists as a small but constant ingredient in the atmosphere; it is also the characteristic element of all organized tissues, whether vegetable or animal. A knowledge of the chemistry of carbon in all its branches is equivalent to an acquaintance with what was formerly styled Organic Chemistry.

Carbon is an **allotropic body**, that is, it exists in various states, which, though chemically the same, are yet, physically, without the least resemblance to each other. There are two great varieties of carbon—crystalline and amorphous.

Crystalline Carbon:—

1. **The diamond.** Although for some time previously the true composition of the diamond had been suspected, it was only at the beginning of the present century that conclusive evidence was obtained. The diamond is now known to be nearly pure carbon, which when burned in an atmosphere of oxygen yields nothing but carbonic anhydride, and leaves a minute ash consisting chiefly of silica and ferric oxide. The specific gravity of the diamond is from 3·5 to 3·55, and thus furnishes an excellent test of genuineness. Heated to about the melting point of silver it blackens, and evolves carbonic anhydride, while it is entirely converted into a coke-like mass by the heating of a powerful galvanic battery. The diamond is the hardest known body, and has to be split and polished by fragments *of itself.* Crystals of the gem, when so set in a handle that an edge where two natural faces of the crystal meet and project from the holder, possess the power of cutting glass. The setting is important, as a splinter from a diamond will only scratch, without cutting.

2. **Graphite**, also called **plumbago** and **black lead**, is a crystalline carbon, containing as a rule more extraneous mineral matter than the diamond. The chief constituent of its ash is iron, the proportion of which varies up to 5 per cent. It is formed artificially during the cooling of ordinary cast iron, and the crystals thus produced are called by iron-workers *kish*. The diamond crystallizes in octahedra (regular system), while graphite is found in six-sided prisms (hexagonal system). The uses of graphite in the arts, in the manufacture of pencils and as a polishing powder for iron, are too well known to require description. It may be noted, that although formerly cut from the solid mineral, pencils are now chiefly made from the powdered graphite puri-

fied from silica, by making it into a paste with certain binding materials, moulding, and drying.

Amorphous carbon is found chiefly as charcoal, lampblack, and coke, and occurs in the Pharmacopœia in three forms.

1. **Wood charcoal** (*carbo ligni*), which is prepared by burning wood in closed retorts out of contact with the air, and is therefore the residue of the destructive distillation of wood. (*See* **Methyl Hydrate** and **Acetic Acid.**) It contains the natural mineral matters of the plants from which it is derived, which are chiefly potassium salts.

Characters.—In black brittle porous masses, without taste or smell, very light, and retaining the shape and texture of the wood from which it was obtained. When burned at a high temperature with free access of air, it leaves not more than two per cent. of ash.

2. **Animal charcoal** (*carbo animalis*) is prepared by the carbonization of bones in closed vessels; it is rich in bone earth (chiefly calcium phosphate). It is, according to the B.P.,—

The residue of bones which have been exposed to a red heat without the access of air. Consists principally of charcoal, phosphate, and carbonate of lime.

3. **Purified animal charcoal** (*carbo animalis purificatus*) is pure carbon obtained by dissolving out the phosphates and other earthy matters from ordinary animal charcoal, by means of dilute hydrochloric acid.

Characters.—The B.P. preparation is a black pulverulent substance; inodorous and almost tasteless. Tincture of litmus diluted with twenty times its bulk of water, agitated with it and thrown upon a filter, passes through colourless. When burned at a high temperature with a little red oxide of mercury and free access of air, it leaves only a slight residue.

When carbon burns in a limited supply of oxygen or air, carbonous oxide (CO) is produced, while in a full supply the resulting gas is carbonic anhydride (CO_2).

COMPOUNDS OF CARBON AND HYDROGEN.

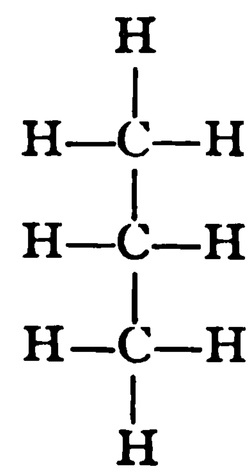
The atom of carbon being a tetrad, can naturally combine with four atoms of hydrogen, thus forming a saturated molecule CH_4 :—

$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$$

The next possible saturated compound would be C_2H_6, because the two carbon atoms in uniting with each other, would each lose one point of their atomicity, thus :—

$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H—C—H \\ | \\ H \end{array}$$

In the same manner the saturated molecule produced from three atoms of carbon would be C_3H_8, thus :—



In this way an endless series of compounds might be produced, each member of the series differing from the one below it by a constant addition of CH_2. Such a series is said to be **homologous** (ὁμὸς, *the same*).

By parting with one or more atoms of their hydrogen, these saturated compounds can give birth to basylous radicals, the atomicity of which is always equal to the number of hydrogen atoms so parted with. Thus CH_4 may give rise to the radical CH_3, which will then act as a monad; also to the radical CH_2, which will act as a dyad; and, lastly, to CH, which will behave as a triad radical.

To enable us readily to remember the composition of any particular radical we use certain typical formulæ, by the aid of which, coupled with a remembrance of the amount of carbon in any radical, we are enabled at once to formulate it correctly. In these typical formulæ, *n* is employed to signify the number of carbon atoms, and we have, for example : C_nH_{2n+2}. Which means, that whatever may be the number of atoms of carbon contained in any member of the homologous series which this formula represents, the atoms of hydrogen will be exactly twice as numerous with two added.

A glance at the following table will show the derivation of some of these radicals, and will also serve to exhibit the system of nomenclature which is followed :—

Saturated Series. C_nH_{2n+2}.	*Monad Series.* C_nH_{2n+1}.	*Dyad Series.* C_nH_{2n}.	*Triad Series.* C_nH_{2n-1}.
CH_4. Methane.	$(CH_3)'$. Methyl.	$(CH_2)''$. Methene (or Methylene).	$(CH)'''$. Methenyl.
C_2H_6. Ethane.	$(C_2H_5)'$. Ethyl.	$(C_2H_4)''$. Ethene (or Ethylene).	$(C_2H_3)'''$. Ethenyl.
C_3H_8. Propane.	$(C_3H_7)'$. Propyl.	$(C_3H_6)''$. Propene (or Propylene).	$(C_3H_5)'''$. Propenyl.

A full study of these bodies will be found in future chapters, together with their many interesting derivatives, including alcohols, ethers, and the so-called organic acids. Meantime it is advisable to obtain a familiarity with the three commoner hydrocarbons to enable the student to understand the composition of ordinary coal gas, which essentially is a mixture of several of them.

METHANE (SYNS. *Marsh Gas. Light Carburetted Hydrogen. Fire Damp*). **Formula, CH_4.**

This is a colourless and almost inodorous gas, which is ***not acted upon by chlorine in the dark***, and burns in the air with a yellow flame, forming carbonic anhydride and water.

$$\underset{2\text{ vols.}}{CH_4} + \underset{4\text{ vols.}}{2O_2} = \underset{2\text{ vols.}}{CO_2} + 2H_2O.$$

It is given off from stagnant pools of water, and is also the dreaded *fire damp* of our coal mines. It constitutes the chief *inflammable* but not the *luminous* portion of coal gas. A litre of it weighs ·71558 gramme; 100 cubic inches weigh 17·41 grains.

It may be prepared by heating sodium acetate with sodium hydrate in the presence of calcium hydrate to prevent fusion (*soda lime*).

$$NaC_2H_3O_2 + NaHO = CH_4 + Na_2CO_3.$$

If the sodium hydrate were used pure, it would fuse and attack the glass.

ETHENE (SYNS. *Ethylene. Olefiant Gas. Heavy Carburetted Hydrogen*). **Formula, C_2H_4.**

Is a colourless gas having a slight smell of garlic. It is nearly insoluble in water, but soluble in alcohol, ether, and volatile and fixed oils. It burns in the air with a very brilliant white light, and is both an inflammable and a luminous constituent of gas. It is very explosive when mixed with air or oxygen :—

$$\underset{2\text{ vols.}}{C_2H_4} + \underset{6\text{ vols.}}{3O_2} = \underset{4\text{ vols.}}{2CO_2} + 2H_2O.$$

It is prepared by heating alcohol with six times its weight of strong sulphuric acid, and passing the gas evolved first through solution of potassium hydrate to absorb carbonic and sulphurous anhydrides, and then through strong sulphuric acid to absorb ether vapour, all of which are simultaneously produced with the ethene. The action is one of simple abstraction of water by the sulphuric acid thus :—

$$C_2H_5HO - H_2O = C_2H_4.$$

When ethene is mixed with chlorine in equal volumes they combine, even in the dark, to form a heavy oily liquid called ethene chloride, $C_2H_4Cl_2$, or *Dutch liquid;* hence the name, olefiant or oil-producing gas.

ETHINE (SYN. *Acetylene*). **Formula, C_2H_2.**

Is a colourless gas, which when mixed with chlorine explodes and deposits carbon, and also burns in the air with a bright smoky flame. It is formed artificially by direct synthesis from its elements by burning an electric light from two carbon points in a current of hydrogen. The battery used must be very powerful, and on passing the resulting gases through a cuprous chloride a red deposit forms, which when treated with hydrochloric acid, yields pure ethine. It is rapidly absorbed by fuming sulphuric acid, and may also be produced by passing a mixture of methane and carbonous oxide through a red-hot tube.

$$\underset{2\text{ vols.}}{CH_4} + \underset{2\text{ vols.}}{CO} = \underset{2\text{ vols.}}{C_2H_2} + H_2O.$$

COAL GAS.

Is prepared by throwing coal into red-hot iron retorts and immediately closing them. The gas produced first passes through coils of pipes to cool it, and cause it to deposit, as *tar*, all the constituents not gaseous at ordinary

temperatures. It is then passed through *purifiers* filled with a mixture of sawdust and moist ferric oxide to absorb impurities such as carbonic anhydride and sulphuretted hydrogen. Finally, it is received into the gasometers, where it is stored over water for use.

The products of coal distillation are usually thus given :—

A. *In the Gas.*	B. *In the Tar, or left in the Purifiers.*
* Olefiant gas, C_2H_4.	Liquid hydrocarbons.
* Acetylene, C_2H_2.	Carbolic acid.
† Marsh gas, CH_4.	Naphthaline, (solid) $C_{10}H_8$.
Hydrogen.	Anthracene, „ $C_{14}H_{10}$.
Nitrogen.	Ammonium salts.
* Vapours of liquid hydrocarbons.	Cyanides.
‡ Carbonous oxide.	Carbonic anhydride.
‡ Carbon disulphide.	Sulphuretted hydrogen.

Good coal gas (issuing from an argand burner at the rate of 5 cubic feet per hour) should have an illuminating power equal to 12 or 14 sperm candles, and should not discolour moist turmeric paper (absence of NH_3) or paper dipped in solution of plumbic acetate (absence of H_2S).

The value of coal gas for illuminating purposes is practically ascertained by comparing its light with that of a sperm candle, in an instrument called a photometer; but a very shrewd estimate of its quality may be made by taking a known volume over mercury and then introducing bromine or fuming sulphuric acid. The greater the contraction of volume which then takes place, the better the gas (*i.e.*, richer in ethene, acetylene, and kindred bodies).

COMPOUNDS OF CARBON WITH OXYGEN,

CARBONOUS OXIDE (SYNS. *Carbonic Oxide. Carbon Monoxide*).

Formula, CO. Molecular Weight, 28. Density, *referred to Hydrogen*, **14. Density,** *referred to Air*, **·968.**

Is produced—

1. By the combustion of carbon in a limited supply of air.
2. By passing carbonic anhydride over red-hot charcoal :—

$$\underset{2\text{ vols.}}{CO_2 + C} = \underset{4\text{ vols.}}{2CO.}$$

3. By heating oxalic acid with sulphuric acid :—

$$H_2C_2O_4 + H_2SO_4 = H_2SO_4H_2O + CO + CO_2\,;$$

and then absorbing the carbonic anhydride by passing the mixed gases through solution of calcium hydrate.

4. By heating crystallized potassium ferrocyanide with ten times its volume of strong sulphuric acid :—

$$K_4FeC_6N_6.3H_2O + 6H_2SO_4 + 3H_2O = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4.$$

It is important not to continue the heating beyond the point sufficient to liquefy the contents of the retort, as the sulphuric acid is reduced to sulphurous anhydride, and carbonous oxide is no longer evolved.

* The most valuable illuminating portions.
† The largest constituent.
‡ The most undesirable impurities.

Carbonous oxide is an exceedingly poisonous gas, colourless, invisible, and scarcely soluble in water. It burns in the air with a blue, lambent flame, producing carbonic anhydride.

It reduces at a red heat many metallic oxides, and it thus plays an important part in the preparation of metals, such as iron, the ores of which are heated in a furnace with coal.

It is absorbed by potassium hydrate, producing potassium formate :—

$$KHO + CO = KCHO_2.$$

But its best absorbent is solution of cuprous chloride, which is therefore the reagent employed for this purpose in gas analysis. Carbonous oxide acts as a dyad radical in displacing the hydrogen of compound radicals, such as ammonia, and is then called **carbonyl.** (*See* **Amides.**)

CARBONIC ANHYDRIDE (Syns. *Carbon Dioxide. Carbonic Acid Gas. Choke Damp*). **Formula, CO_2. Molecular Weight, 44. Density,** *referred to Hydrogen*, **22. Density,** *referred to Air*, **1·524.**

Is prepared :—

1. By burning carbon in a full supply of oxygen.
2. By the action of an acid upon a carbonate :—

$$CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

It is given off in great abundance from volcanoes, and also in certain fissures in volcanic regions, notably the *Grotto del Cane* in Italy. It is the invariable product of the burning of vegetable and animal matters in the air, and is the *choke damp* which collects in mines after an explosion. Carbonic anhydride is colourless, incombustible, and much heavier than air. It is soluble in water, and also to some slight extent in alcohol; and when prepared for use should be collected by displacement. (*See* **Chlorine.**) Atmospheric pressure greatly increases the solubility of carbonic anhydride in water, of which the ordinary aerated waters are examples. Carbonic anhydride may be liquefied by a pressure of 36 atmospheres at 32° F., and the resulting fluid will solidify by the cold produced by its own evaporation as it issues from a small jet into a metallic cylinder. Liquid carbonic anhydride, mixed with ether, creates an intense degree of cold. The solution of carbonic anhydride in water is viewed as being carbonic acid, H_2CO_3, but that body has not been isolated, owing to the great readiness with which it decomposes. Such solution possesses a sharp taste, and is acid to test-paper. It is the acid which gives rise to the class of salts called **carbonates.** The carbonates of ammonium, sodium, and potassium are soluble in water; that of lithium is sparingly so, and the remaining metallic carbonates are insoluble.

All carbonates effervesce with acids, giving off carbonic anhydride, and when heated to dull redness become converted into oxides, except the carbonates of calcium, barium, and strontium, which require continued bright-red heat, and those of sodium and potassium, which are not decomposed by heat. Solutions of soluble carbonates precipitate most metals from their solutions, either in the form of carbonates, hydrocarbonates, or simple hydrates. The first variety of precipitate is produced in solutions of calcium, barium, strontium, silver, lead, and mercury; the second, in solutions of magnesium, zinc, copper, ferrous iron, and bismuth; the third, in solutions of aluminium, ferric iron, chromium, and antimony.

METALLIC CARBONATES

LITHIUM CARBONATE (Syn. *Lithii Carbonas*). **Formula, Li_2CO_3.**

Is produced by mixing strong solutions of lithium chloride (or sulphate) and ammonium carbonate:—

$$2LiCl + (NH_4)_2CO_3 = Li_2CO_3 + 2NH_4Cl.$$

In consequence of lithium carbonate being soluble to the extent of about 1 per cent. in water at 60° F., it cannot be procured in a very pure state by this method, as, if it is washed much, a considerable waste is incurred. It is therefore more advisable to begin by converting lithium sulphate into lithium acetate by double decomposition with barium acetate. The solution, after filtration and evaporation, yields lithium acetate in a solid condition, and upon heating this until the residue is white, it is converted into carbonate.

The B.P. thus describes the salt:

Characters and Tests.—In white powder or in minute crystalline grains, alkaline in reaction, soluble in 100 parts of cold water, insoluble in alcohol. It dissolves with effervescence in hydrochloric acid.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 94.)

A solution of this salt of ½ per cent. strength exhibits the reaction of an alkali. A hot saturated solution will deposit the anhydrous carbonate by slow evaporation. In some respects it resembles sodium hydrocarbonate. Dissolved in water in the proportion of half a grain per ounce, and the solution saturated with carbonic anhydride at a pressure of about 100 pounds per square inch, the resulting solution is *liquor lithiæ effervescens*, B.P. On account of the small atomic weight of lithium, a little of its carbonate will perform the same office as a much larger amount of sodium or potassium carbonate. This property and the ready solubility of the salt it forms with uric acid (lithium urate) are the reasons for the introduction of lithium salts into medicine.

The B.P. thus describes the manufacture of *liquor lithiæ effervescens*:—

Take of—

Carbonate of Lithia . .	10 grains.
Water	1 pint.

Mix in a suitable apparatus, and pass into it as much pure washed carbonic acid gas, obtained by the action of sulphuric acid on chalk, as can be introduced with a pressure of seven atmospheres. Keep the solution in bottles securely closed, to prevent the escape of the compressed gas.

Characters and Tests.—Effervesces strongly when the containing vessel is opened, carbonic acid gas escaping. The liquid is clear and sparkling, and has an agreeable acidulous taste. Half a pint of it, evaporated to dryness, yields five grains of a white solid residue, answering to the tests for carbonate of lithia.

AMMONIUM CARBONATE (Syns. *Carbonate of Ammonia. Diammonium Carbonate*). **Formula, $(NH_4)_2CO_3$.**

Has not been isolated. The ordinary carbonates containing a larger percentage of the carbonate radical. It is supposed to exist in *spiritus ammoniæ aromaticus*, being formed by the action of the ammonium hydrate on the official carbonate, thus:—

$$N_4H_{16}C_3O_8 + 2NH_4HO = 3(NH_4)_2CO_3 + H_2O.$$

In practice, however, it contains a slight excess of ammonium hydrate, owing to some of the bicarbonate remaining in the retort

AMMONIUM-HYDROGEN CARBONATE (SYNS. *Bicarbonate of Ammonia. Acid Carbonate of Ammonia. Ammonium Bicarbonate. Hydric Ammonic Carbonate*). **Formula, NH_4HCO_3.**

Is prepared by saturating ammonium hydrate with carbonic anhydride. The ordinary *carbonate of ammonia* of the shops, when exposed to the air, is slowly converted into this salt, which has a less ammoniacal odour than the other compounds of ammonium and the carbonate radicals. It can be separated from the carbonate above described by treatment with alcohol of 90 per cent. strength, in which it is insoluble, while the ammonium carbonate dissolves.

TETR-AMMONIUM CARBONATE (SYNS. *Sesqui Carbonate of Ammonia. Ammoniæ Carbonas*). **Formula, $N_4H_{16}C_3O_8$. Molecular Weight, 236.**

Commercial *carbonate of ammonia* consists essentially of this salt. It is prepared by heating together calcium carbonate and ammonium chloride or sulphate, until no more tetr-ammonium carbonate sublimes; when the following reaction probably takes place:—

$$3(NH_4)_2SO_4 + 3CaCO_3 = N_4H_{16}C_3O_8 + H_2O + 2NH_3 + 3CaSO_4.$$

The salt is found sufficiently pure in commerce for all pharmaceutical purposes, and the manufacture on the small scale is troublesome. It is met with in translucent crystalline masses, with a strong ammoniacal odour and alkaline reaction; soluble in cold water, more sparingly in spirit. It volatilizes entirely when heated, and is readily dissolved by acids with effervescence.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 94.)

$$\left.\begin{matrix}\text{20 grains of}\\ \text{Carbonate of Ammonia}\end{matrix}\right\}\text{ neutralize }\left\{\begin{matrix}23\tfrac{1}{2}\text{ grains Citric Acid}\\ 25\tfrac{1}{2}\text{ grains Tartaric Acid}\end{matrix}\right.$$

The formula $N_4H_{16}C_3O_8$ must be regarded as purely empirical, being really composed of one molecule of **ammonium carbamate** ($N_2H_6CO_2$), and two of **ammonium-hydrogen carbonate** (NH_4HCO_3). The carbamate is regarded as derived from diammonium carbonate by the abstraction of the elements of water, which body is easily and quietly taken up again on exposing the carbamate to its action. Tetr-ammonium carbonate does not dissolve in water without decomposition. If the powdered salt be stirred up with water, and the solution after a few seconds poured off, the residue will be tolerably pure ammonium-hydrogen carbonate.

Carbamates may be viewed as being derived from an acid called carbamic, which has not been isolated. The formula of this acid is considered to be HNH_2CO_2, or,—

$$CO\left\{\begin{matrix}OH,\\ NH_2\end{matrix}\right\}\text{ which yields by displacement of H by ammonium, } CO\left\{\begin{matrix}ONH_4\\ NH_2\end{matrix}\right.$$

The formula of ammonium carbamate is therefore $NH_4NH_2CO_2$, or empirically $N_2H_6CO_2$, and the whole molecule of commercial *carbonate of ammonia* is thus constituted:—

$$\begin{array}{ll}\left.\begin{matrix}NH_4HCO_3\\ NH_4HCO_3\end{matrix}\right\} & \text{Two molecules ammonium-hydrogen carbonate.}\\ N_2H_6\ CO_2 & \text{One molecule ammonium carbamate.}\\ \hline N_4H_{16}C_3O_8 & \end{array}$$

The strong odour of the commercial carbonate is due chiefly to the presence of carbamate.

The affinities and analogies of ammonium carbonate are numerous. Through ammonium cyanate it has affinity with cyanates generally, and also with sulphocyanates. (*See* **Cyanogen.**) Thus substances between which there were formerly supposed to be no noticeable resemblance, are now seen to be members of greatly similar (in some cases identical) series.

In practice, the manufacture of tetr-ammonium carbonate is sometimes conducted by the dry distillation of any animal matter. If produced in this manner, it requires purification, which is carried out by re-subliming the impure salt with the charred material left in the retort after the evolution of vapour has entirely ceased. It is best to condense the sublimate in an earthen or glass receiver, but lead is sometimes employed. The chief probable contaminations are ammonium sulphate, ammonium chloride, calcium hydrate, calcium chloride, lead, and rarely ammonium hyposulphite.

By the evaporation of a solution of the commercial salt in *liquor ammoniæ*, the pure tetr-ammonium carbonate is procured, the crystals of which are transparent and prismatic. These decompose into ammonium hydrogen carbonate upon exposure to the air much more readily than the fibrous opalescent masses in which the salt exists in commerce. In consequence of ammonium carbamate being more volatile than ammonium carbonate it is dissipated before the latter; and therefore, after exposing commercial *sesquicarbonate* to the air for some time, the residue receives the name of "mild carbonate of ammonia," and its vapour, which only comes off slowly, is very feebly alkaline to red litmus paper. The solution in dilute acids should be perfectly colourless, otherwise contamination with oily empyreumatic products is indicated.

SODIUM CARBONATE (SYNS. *Sodæ Carbonas. Subcarbonate of Soda. Soda. Disodic Carbonate*) **Formula, Na_2CO_3. Molecular Weight, 106. Formula, when crystallized, $Na_2CO_3.10H_2O$.**

This highly important salt is found in nature in an impure state. It is of interest, not only in its pharmaceutical and chemical relations, but also in dyeing, glass-making, and many other branches of the industrial arts. The natural sources from which sodium carbonate may be procured by merely physical processes are: 1. The "soda lakes of Egypt and Hungary." 2. The Icelandic hot springs, believed to be of volcanic origin. 3. Certain plants found near the sea-shore in Spain and some other countries, which yield the ash known as *barilla*. 4. As a substance found solid in various countries, and termed *natron*, in which form it is contaminated with sodium sulphate and other salts of sodium. Sodium carbonate is also a constituent of *kelp*, and crystallizes out during the evaporation of the solution, together with the other sodium salts.

Almost the entirety of the enormous quantity of sodium carbonate at present consumed, is produced by a modification of Leblanc's original process. There are three distinct steps.

The first stage consists in decomposing sodium chloride (6 parts) by means of sulphuric acid (10 parts). The bye-product is hydrochloric acid, which must be condensed as before directed. (*See* **Hydrochloric Acid.**)

The second stage consists in the conversion of 35 parts of sodium sulphate (formed in the last process) into sodium carbonate by the joint action of calcium carbonate (4 parts) and carbon, in the form of small coal or coke dust, at a high temperature.

1. $H_2SO_4 + 2NaCl = Na_2SO_4 + 2HCl.$

2. $Na_2SO_4 + 2CaCO_3 + 2C_2 = Na_2CO_3 + CaO.CaS + CO_2 + 4CO.$

The third stage is the purification of the hard dark-coloured product (termed *black ash soda*) by pulverization disintegration by means of steam and lixiviation of the resulting mass with water.

For the sake of economy it is customary not to attempt to dissolve the sodium carbonate in pure water, but to use a nearly saturated solution obtained from a previous treatment. Thus a much less quantity of water will have to be removed by evaporation. On applying heat until the dry salt, in consequence of frequent stirring, is obtained in the form of a coarse powder, a residue termed *soda salt* remains. But this is not generally pure enough to be redissolved and crystallized without further treatment. The usual course pursued in order to decompose and remove impurities consists in roasting four parts with one part of sawdust. Thus the sodium sulphide contained in the *soda salt* is converted by the elimination of sulphuretted hydrogen into sodium oxide, which with the carbonic anhydride, produced by the combustion of the sawdust, forms sodium carbonate.

Commercial *soda*, as it is commonly called, ordinarily occurs in crystals. These are formed by dissolving the purified *soda salt* in hot water, and removing the solution after subsidence into crystallizing pans, constructed of such a shape that a large surface shall be exposed to the air. The formula of the crystals is $Na_2CO_3, 10H_2O$.

Sodæ Carbonas is usually met with in transparent colourless laminar crystals of a rhombic shape, efflorescent, with a harsh alkaline taste and strong alkaline reaction. By heat they undergo aqueous fusion, and then dry up, losing 63 per cent. of their weight.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 95.)

20 grains of Carbonate of Soda	neutralize	9·7 grains Citric Acid, or 10·5 grains Tartaric Acid.

If a sample be found impure, the most ready mode of purification is to make a hot saturated solution, and whilst it is cooling agitate constantly and quickly. By this means the sodium carbonate is obtained in a coarse crystalline powder, whilst much of the contaminating salts remains in solution, and the greater part of those adherent to the crystals may be removed by shaking with cold water and pouring off the solution.

Sodæ carbonas exsiccata, B.P., is simply the crystals from which water (to the extent of 63 per cent.) has been removed by heat. Water at 212° F. dissolves fully $1\frac{1}{4}$ times its weight of the crystals, but only about 47·6 per cent. of this powder; whilst at 60° F. it takes up 50 per cent. of the hydrated and 21·8 per cent. of the anhydrous salt. The point of greatest solubility appears to be a little below 100° F. The desiccated salt forms several hydrates in contact with water, heat being in all cases rendered perceptible.

The powder formed by the efflorescence of crystals of sodium carbonate in the air is $Na_2CO_3, 5H_2O$. If the temperature be raised to about 100° F. this powder loses more water, being converted into $Na_2CO_3.H_2O$. These hydrates may also be formed by moistening the anhydrous salt with a little water: crystals having 7, 8, 9, and 15 H_2O are also obtainable.

(For another process by which Na_2Co_3 is made, see **Sodium**.)

SODIUM HYDROGEN CARBONATE. (SYNS. *Bicarbonate of Soda. Sodium Bicarbonate. Sodium Acid Carbonate. Hydric Sodic Carbonate.*) **Formula, $NaHCO_3$. Molecular Weight, 84.**

This salt is manufactured on the large scale by passing a stream of carbonic anhydride through a mixture of two parts of the crystallized and three of the anhydrous sodium carbonate. The carbonic anhydride is absorbed and

sodium hydrogen carbonate is produced in the form of small crystalline particles. The reaction is:—

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

The employment of a proportion of anhydrous carbonate is necessary, because it is desired to obtain a remunerative product in a pulverulent form. If no other than the crystallized salt be employed, as the carbonic anhydride is passed, the mixture becomes liquid, and the hydrogen carbonate afterwards only partially deposits in transparent crystals, much of the product remaining in solution which cannot be evaporated without decomposition. In practice the passing of CO_2 is continued until a little of the product dissolved in *cold* water ceases to give a red precipitate with mercuric chloride, showing that the carbonate has been entirely converted.

Sodæ bicarbonas is met with in powder or small opaque irregular scales, white, of a saline not unpleasant taste.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 95.)

20 grains of Bicarbonate of Soda } neutralize { 16·7 grains of Citric Acid, or 17·8 grains Tartaric Acid.

The salt constitutes the alkaline portion of several mineral waters. A mode of manufacture of great practical and theoretical interest is to take advantage of the double decomposition between solid tetr-ammonium carbonate and a solution of sodium chloride. A solution of the latter in three parts of water is stirred up with one part of the *sesquicarbonate of ammonia* of commerce. After the mixture has been allowed to react for five or six hours, the sodium hydrogen carbonate deposits in small particles. The following is the reaction:—

$$H_2O + N_4H_{16}C_3O_8 + 2NaCl = 2NaHCO_3 + 2NH_4Cl + (NH_4)_2CO_3.$$

Ammonium chloride and ammonium carbonate, being considerably more soluble than the sodium hydrogen carbonate, remain in solution. The objection to this mode of preparation is, that a variable quantity of sodium chloride is carried down, which cannot be entirely removed from the product without great loss. When the hydrogen carbonate is heated it begins to lose carbonic anhydride and water at (or even below) 160° F. At a red heat nothing remains but sodium carbonate in an anhydrous condition. When a solution is boiled for a long time, pure sodium carbonate is the only salt left in the liquid. At 60° F. the strongest solution of sodium hydrogen carbonate which can be made will contain 1 of the salt in 9½ of water. The solubility of the salt in water at high temperatures (such as 120° to 212° F.) cannot be accurately determined because of the readiness with which it commences to decompose.

TETRA-SODIUM CARBONATE (SYN. *Sesquicarbonate of Soda*). **Formula, $Na_4H_23CO_3$.**

Occurs in the form of *Trona* in Africa. It is undoubtedly a combination of the two preceding substances, formed as shown below:—

$$Na_2CO_3 + 2NaHCO_3 = Na_4H_23CO_3.$$

The native salt contains $2H_2O$ (as water of crystallization). That these two salts are chemically united, is proved with tolerable certainty by the fact that a 10 per cent. solution of magnesium sulphate does not lose its limpidity upon the addition of a saturated solution of tetra-sodium carbonate. Water at 60° F. takes up about 16·8 per cent.

POTASSIUM CARBONATE (SYNS. *Subcarbonate of Potash. Potassæ Carbonas. Dipotassic Carbonate. Salts of Tartar*). **Formula, K_2CO_3. Molecular Weight, 138.**

Is not a natural product, but is readily procured, though in a very impure form, by calcining plants and vegetable substances. Upon lixiviating the ash, potassium carbonate, together with some potassium sulphate and potassium chloride, are separated in solution, whilst aluminous matter, silicic anhydride, calcium carbonate, and calcium phosphate, remain undissolved. On evaporating the solution, a residue commercially termed *crude potash* is obtained. In order to convert this into the tolerably pure form of potassium carbonate known as *pearlash*, and mentioned in the B.P. as the source of the official salt, it is necessary to digest with an equal weight of water for about a week, and to evaporate the clear decanted liquid with constant stirring until crystalline grains are left. These may be washed with a nearly saturated solution of the pure salt, dried, and fused in iron pots.

As it is easier to burn wood than the leaves and succulent portions of plants, wood ashes are the practical sources of potassium carbonate, especially since, even if the other portions could be economically burnt, the mineral residue would be so light as to be blown away should any wind prevail at the time of the combustion. For though the process is conducted in as sheltered spots as convenient, or in excavations purposely made, it is almost impossible to secure the entire absence of loss, even in the case of wood.

The carbonate is derived from the malates, tartrates, oxalates, and other organic salts of potassium contained in plants. It has been observed that the yield of potassium carbonate depends greatly upon the woody or herbaceous nature of the vegetable substances used in its production; the latter, in consequence of the liquid portion (*i.e.* the sap) containing the salts, being the most abundant source. The less compact portions of the same plant also yield more than the hard and close-textured. North America and Russia export a large quantity of *potash* and *pearlash*.

Potassæ carbonas is described in the B.P. as K_2CO_3 with about 16 per cent. of water of crystallization.

Obtained from commercial pearlash, the product of lixiviation of wood ashes, by treating the pearlash with its own weight of distilled water, and evaporating the solution so formed to dryness, while it is kept briskly agitated.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 95.)

The B.P. describes the pure salt as follows:—

Characters and Tests.—A white crystalline powder, alkaline and caustic to the taste, very deliquescent, readily soluble in water but insoluble in spirit, and effervescing with diluted hydrochloric acid. Loses about sixteen per cent. of its weight when exposed to a red heat.

$$\left.\begin{array}{c}\text{20 grains}\\\text{Carbonate of Potash}\end{array}\right\}\text{ neutralize }\left\{\begin{array}{l}\text{17 grains Citric Acid, or}\\\text{18 grains Tartaric Acid.}\end{array}\right.$$

A boiling saturated solution forms crystals of the formula $K_2CO_3.2H_2O$, which are octahedra and extremely deliquescent. They only contain 4 per cent. more water than the B.P. pulverulent salt. Water at 60° F. dissolves about 1·18 times its weight of the dry carbonate. When a current of steam passes over the salt heated to incipient fusion, carbonic anhydride passes off, potassium hydrate remaining. The decomposition, however, is never complete.

There are many other sources from which potassium carbonate in a pure condition may be procured: for example, when potassium oxalate or quadroxalate is heated the carbonate left is free from uncombined carbon, and all

but mere traces of salts. Potassium hydrogen tartrate also yields potassium carbonate when it is calcined. In this case, however, the residue contains free carbon, which on treatment with water remains insoluble, and may be filtered out. A very pure form of the carbonate may likewise be obtained by calcining potassium hydrogen carbonate in a silver crucible.

POTASSIUM HYDROGEN-CARBONATE (SYNS. *Potassæ Bicarbonas. Mono-Potassic Carbonate. Potassium Acid Carbonate*). **Formula, $KHCO_3$. Molecular Weight, 100.**

Is prepared by saturating an aqueous solution of potassium carbonate with carbonic anhydride.

Crystals separate after some days; but the solution must not be evaporated at 212° F., as some amount of decomposition would then occur. When it is requisite to entirely prevent decomposition, 100° F. is the limit of maximum safety and rapidity. In consequence of the less ready combination of potassium carbonate than of sodium carbonate with carbonic anhydride, and of the desirability of procuring the hydrocarbonate in large crystals, the carbonate is dissolved in water, instead of being (as in the case of the sodium salt) treated in the solid state.

The decomposition which takes place is:—

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3.$$

The characteristics of the salt are as subjoined:—

Colourless right rhombic prisms, not deliquescent, of a saline feebly alkaline taste, not corrosive. Diluted hydrochloric acid causes strong effervescence.

(*For analysis, see Author's* **Analytical Chemistry**, page 95.)

$$\left.\begin{array}{c}\text{20 grains}\\ \text{Bicarbonate of Potash}\end{array}\right\}\text{ neutralize }\left\{\begin{array}{l}\text{14 grains Citric Acid, or}\\ \text{15 grains Tartaric Acid.}\end{array}\right.$$

Only a very small quantity dissolves in boiling alcohol, and still less in cold. It behaves like sodium hydrogen-carbonate as regards magnesium sulphate.

When subjected to a high temperature it undergoes the same decomposition as the corresponding sodium compound. It is neither deliquescent nor efflorescent, in the latter respect differing from the sodium carbonate.

Water at 60° F. dissolves (approximately) 25·5 per cent. This being less than the solubility of potassium carbonate in water, explains the fact that on passing carbonic anhydride into a saturated solution of that salt, crystals of the compound resulting from its action are deposited. It is a solvent of uric acid, hence it is used in medicine for that purpose (in *lithiasis*). With the salts of several metals it combines to give birth to double carbonates, such as the magnesium potassium-carbonate. It is a slight solvent of metallic iron when a solution is boiled in vessels of that metal.

TETRA-POTASSIUM CARBONATE (SYN. *Sesquicarbonate of Potash*). **Formula, $K_4H_2.3CO_3$.**

The existence of this salt is not definitely determined. It is constituted like the sodium salt, and is said to separate on crystallizing a mixture of 79 of potassium carbonate and 100 of potassium hydrogen-carbonate.

ARGENTIC CARBONATE. Formula, Ag_2CO_3.

When free from alkaline salts, this is a yellow powder, which blackens on exposure to light. It constitutes the white precipitate produced on adding

potassium carbonate to argentic nitrate. Ammonium hydrate takes it up with ease, and on heating to 480° F. leaves the pure metal; but provided the temperature does not exceed 390° F., argentic oxide remains.

CALCIUM CARBONATE (SYNS. *Chalk. Calc-spar. Carbonate of Lime. Limestone. Marble. Arragonite*). **Formula, $CaCO_3$. Molecular Weight, 100.**

Is the most abundant and valuable natural salt of calcium. It is secreted by many of the lower classes of animals to form their shell. It may be obtained in a condition absolutely free from contamination by dissolving marble or any similar variety of the salt in hydrochloric acid, and after throwing down the aluminium, iron, magnesium, and the phosphates of the same by means of calcium hydrate, and filtering, neutralizing the filtrate with ammonium carbonate. By this method a white powder is produced which requires drying at 400° to 500° F. When thrown down from cold solutions, calcium carbonate is amorphous, but on being kept under water it assumes the crystalline state. With hot solutions the precipitate is at once produced as minute crystals.

The action upon neutral litmus paper is very feebly alkaline. When heated in hermetically sealed iron vessels it fuses, and a marble-like solid is found on opening the tube after cooling. It dissolves much more readily in water in presence either of ammoniacal salts or carbonic anhydride. The official forms are :—

1. **White marble** (*marmor album*, B.P.) which is stated to be—

Hard, white, crystalline native carbonate of lime, in masses.

Used in producing carbonic acid gas, and should be the Carrara or *statuary* marble.

2. **Chalk** (*creta*, B.P.) which is—

Native friable carbonate of lime. The native chalk may be employed to yield carbonic acid gas, but is less useful than marble because it does not act so regularly, and forms a frothy mixture; also a large bulk must be used because its specific gravity is much less.

3. **Prepared Chalk** (*creta preparata*, B.P.).

Chalk, freed from most of its impurities by *elutriation*, and afterwards dried in small masses, which are usually of a conical form. Elutriation (*eluo*) is the process of purifying a substance insoluble in water, by washing and straining.

It possesses the subjoined qualities.

A white amorphous powder, effervescing with acids, and dissolving with only a slight residue in diluted hydrochloric acid. It is perfectly amorphous.

4. **Precipitated chalk** (*calcis carbonas precipitata*, B.P.) is directed to be prepared by mixing calcium chloride and sodium carbonate, collecting, washing, and drying the precipitate.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$

It is a white crystalline powder, insoluble in water, dissolving in hydrochloric acid with effervescence.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 96.)

There is a crystallized form of calcium carbonate known as *hydrocalcite*, containing $5H_2O$, and a compound sometimes denominated "calcium orthocarbonate," Ca_2CO_4. The latter is supposed to be derived from the acid H_4CO_4, which is termed *orthocarbonic*. The ordinary and normal acid, H_2CO_3 is, under this theory, looked upon as metacarbonic acid; chalk, with the other forms of normal calcium carbonate, is called *calcium metacarbonate*.

The fact that this body, which is the result of heating chalk or marble in powder to low redness, produces a hydrate with the water, even though its formation be not attended by the evolution of great heat, seems to countenance the idea that it is composed of a mixture of carbonate and oxide; in other words, is an oxy carbonate, forming with water a hydrato-carbonate.

The composition, in accordance with this view, would be:

$$CaCO_3.CaO = Ca_2CO_4.$$

And the proportions of the hydrated salt of hydrato-carbonate =

$$Ca_2CO_4 + H_2O = CaCO_3.Ca2HO.$$

CALCIUM HYDROGEN-CARBONATE (Syns. *Bicarbonate of Lime. Calcium Acid Carbonate*). **Formula, CaH_22CO_3.**

The existence of this salt has been inferred for many years, but it has never been actually obtained. It is supposed to be formed when calcium carbonate is dissolved in water containing carbonic acid. It is of great importance from a pharmaceutical as well as interesting from a general standpoint. By boiling it redeposits the carbonate. Water fully charged with carbonic anhydride dissolves only ·07 per cent. of calcium carbonate, hence it requires extremely dilute solutions of potassium hydro- (or sodium hydro-) carbonate and a soluble salt of calcium to give no visible reaction. Water charged as above has the capability of dissolving out calcium oxide from calcium silicate. Thus it disintegrates calcareous rocks, and when the solution comes in contact with solid bodies it deposits calcium carbonate of more or less purity, according to the nature and amount of the matters mechanically carried down.

The presence of calcium in this form imparts to spring and river water the quality known as *temporary hardness*, because it is removed by boiling.

(*See Water Analysis in Author's* **Analytical Chemistry**, *page* 187.)

The calcium carbonate let fall on subjecting a solution of the hydro salt to the action of a high temperature, constitutes one of those troublesome and dangerous deposits—boiler incrustations.

In the presence of ammonium chloride no precipitate is caused by boiling a solution of calcium hydrogen carbonate.

BARIUM and STRONTIUM CARBONATES. Formulæ, $BaCO_3$ *and* $SrCO_3$.

These bodies are sometimes employed as the sources of the other barium and strontium salts, but do not yield such pure products as the sulphates. In qualitative analysis, barium and strontium are precipitated as carbonates on adding ammonium carbonate to their solutions. When the hydrates are brought in contact with carbonic anhydride, or the oxides with water and the same, the result is the formation of barium and strontium carbonates.

Advantage has been taken of the fact that oxalic acid in solution, added to a liquid containing salts of lime and baryta, precipitates the whole of the lime *immediately*, the baryta being only affected after some time. Witherite, dissolved in water and hydrochloric acid is thus treated. About thirty grains of oxalic acid are sufficient for one pound. The lime precipitate having been eliminated, to the clear filtered solution caustic soda is added. After an hour's rest, filter again and treat the liquid with a solution of sodium carbonate. Collect and wash the precipitate in the usual manner.

Barium carbonate is poisonous, and is occasionally used as a vermin destroyer. Strontium carbonate is quite innocuous except in large quantities in the presence of acids. The barium salt only is transformed into sulphates

by cold alkaline sulphates in solution. Neither give up carbonic anhydride so readily as calcium by the influence of heat. Steam, at a red heat, converts them into oxides or hydrates. The native barium carbonate is *witherite*; native strontium carbonate is *strontianite*.

MAGNESIUM CARBONATE. Formula, $MgCO_3$.

Exists in nature as the minerals termed *magnesite* (tolerably pure), *hydromagnesite* (united with hydrate), and *dolomite* (combined with calcium carbonate). Unlike most other carbonates, it cannot be produced by precipitating a magnesium solution by an alkaline carbonate, as the oxy- or hydrato- carbonate is more stable.

If, however, the carbonic anhydride be passed into water, in which the magnesium hydrato-carbonate is kept suspended by brisk agitation, the hydrate is converted into carbonate, which may be separated in minute crystals by evaporation. Sodium carbonate heated with crystallized magnesium sulphate in a closed vessel gives the pure magnesium carbonate.

Both the ordinary hydrato-carbonate and the pure carbonate dissolve more readily in aqueous carbonic acid than in water.

MAGNESIUM HYDRATO-CARBONATE (MAGNESIUM OXY-CARBONATE)
(SYNS. *Magnesiæ Carbonas. Magnesiæ Carbonas Levis. Magnesia Alba*).
Formula, $(MgCO_3)_3MgO.5H_2O$; *or, better*, $(MgCO_3)_3Mg2HO4H_2O$.

This is the official salt, prepared in two forms, both of which possess absolutely the same composition. *Magnesiæ carbonas levis* is produced from cold dilute solutions of magnesium sulphate and sodium carbonate, and *magnesiæ carbonas* from strong hot solutions of the same.

The following is a representation of the reaction:

$$4MgSO_4 + 4Na_2CO_3 + 5H_2O = (MgCO_3)_3Mg2HO.4H_2O + 4Na_2SO_4 + CO_2.$$

In order to secure the most *ponderous* product, it is requisite to evaporate the solutions after mixing them to perfect dryness, and then dissolve out the soluble portion with hot water. To obtain a result of the utmost lightness it has been advised to subject the moist precipitate, after washing, to a temperature not exceeding 30° F., whereby the water is frozen. On allowing the mass to melt, and then drying as usual, there results a product of even greater levity than the *levis* of the B.P.

Both *magnesiæ carbonas* and *magnesiæ carbonas levis* are white powders the former amorphous and the latter in part crystalline. They are practically insoluble in water unless it contains much CO_2 dissolved, and when heated give off carbonic anhydride and water, leaving the oxide without any change of colour. Both are soluble in acids with effervescence.

(*For analysis, see Author's* **Analytical Chemistry,** *page* 96.)

The liquid known as **fluid magnesia** (*liquor magnesiæ carbonatis*, B.P.), and consisting of a solution of magnesium oxy-carbonate in water charged with carbonic anhydride, may be regarded as probably containing magnesium hydrogen-carbonate, MgH_22CO_3. In default of the existence of this body, which is by no means certain, it undoubtedly is a solution of magnesium carbonate with excess of the carbonic gas. On exposure to light and air the excess of carbonic anhydride passes off and crystals of the carbonate are deposited, having the formula $MgCO_35H_2O$.

ZINC CARBONATE (SYN. *Calamine*). **Formula, $ZnCO_3$.**

Has not been thoroughly investigated. It may probably be procured by

the same methods as magnesium carbonate. Is formed during the preparation of the next salt, but immediately splits up.

ZINC HYDRATO-CARBONATE (ZINC OXY-CARBONATE) (Syns. *White Zinc* [incorrect] *Zinci Carbonas Prepared Calamine Lapis Calaminaris*). **Formula, $ZnCO_3(ZnO)_2 3H_2O$, *or, better*, $ZnCO_3(Zn2HO)_2H_2O$.**

Occurs native as *zinc bloom*, which, however, is not always pure white in colour. It is also prepared by precipitating a solution of zinc sulphate with sodium carbonate, as represented in the equation

$$3ZnSO_4 + 3Na_2CO_3 + 3H_2O = ZnCO_3(Zn2HO)_2 H_2O + 3Na_2SO_4 + 2CO_2.$$

Zinci carbonas, B.P., is a white, tasteless, inodorous powder, insoluble in water; soluble, with effervescence and without residue, in dilute acids.

At 390° F., it evolves carbonic anhydride and water, zinc oxide remaining, which is yellow while hot but white on cooling.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 96.)

The impure native form, known as *calamine*, does not decompose under 570° F., and only slowly at that temperature.

PLUMBIC CARBONATE (Syns. *Ceruse. Cerusite. Carbonate of Lead*). **Formula, $PbCO_3$.**

Cannot be formed by acting upon a plumbic salt with an alkaline carbonate, the precipitate thus formed containing some hydrate, and being

PLUMBIC HYDRATO-CARBONATE (or OXY-CARBONATE) (Syn. *White Lead*). **Formulæ, $2PbCO_3.Pb2HO$, *or* $2PbCO_3 PbO H_2O$.**

It is rarely made in this manner; a more ready and valuable product being obtainable by less expensive methods.

At one time this salt was extensively made by passing a current of carbonic anhydride through a solution of plumbic oxyacetate. The neutral acetate remains in solution, the oxide dissolved being alone precipitated. This acetate on being digested with plumbic oxide, takes up a quantity of the latter, which may again be transformed into carbonate, a portion of plumbic acetate thus serving continuously as a means of causing plumbic oxide to enter into rapid combination with carbonic anhydride. Another mode is to expose sheets of lead to the simultaneous influence of carbonic anhydride, aqueous vapour, and acetic acid. The latter, of about half the strength of vinegar, is placed in small earthenware vessels in the midst of heaps of decaying matter, such as the exhausted bark used in tanning, which give off abundance of carbonic acid gas. Over these pots are laid the sheets of metal so that both the carbonic and acetic vapours may have access to the same surface. The temperature of the tan should approximate to 145° F., and the fermentative decomposition which it undergoes will suffice to maintain the mass at about this degree.

The B.P. description is:—

A soft heavy white powder, blackened by sulphuretted hydrogen, insoluble in water, soluble with effervescence in diluted acetic acid without leaving any residue. Heated to redness it becomes deep yellow being converted into **plumbic oxide.**

(*For analysis, see Author's* **Analytical Chemistry**, *page* 97.)

Sometimes lead shavings are used. In any case the *white lead* requires

grinding. The pasty form used by gasfitters, is manufactured by simply rubbing about 14 parts with 1 part of linseed oil.

Some samples of plumbic oxy- or hydrato-carbonate contain a rather larger proportion of carbonate than that we have given.

CUPRIC CARBONATE. Formula, $CuCO_3$.

Is not known. The carbonates existing in nature are:—

1. Malachite, dicupric oxy- (or "ortho") carbonate: $Cu_2CO_4 + H_2O$.
2. Azurite, tricupric oxy- (or "ortho") carbonate: $Cu_3H_2(CO_4)_2$.

The formulæ may be stated:—

$$1.\ Cu_2CO_4 + H_2O = CuCO_3.Cu2HO.$$
$$2.\ Cu_3H_2(CO_4)_2 = 2CuCO_3.Cu2HO.$$

The former is that obtained on subjecting cupric sulphate to precipitation by an alkaline carbonate, and drying at a gentle heat. At 390° F. it leaves cupric oxide by the evolution of carbonic anhydride and moisture. The mineralogical and technical names for the first salt are, *Atlas ore, green carbonate of copper*, and *mountain green*. Of the second, *Chessy copper, blue malachite, saurite, blue carbonate of copper*, and *blue verditer*.

MERCUROUS CARBONATE. Formula, Hg_2CO_3.

Is of a black or yellow colour, and is produced by the double decomposition between potassium carbonate and a soluble mercurous salt. Mercuric carbonate ($HgCO_3$) cannot be formed from mercuric chloride, nor from mercuric nitrate in the presence of a chloride, by hydrogen-carbonates or carbonates, but an oxycarbonate can be produced by the latter. In consequence of the oxychloride thrown down by hydrogen-carbonates being white in colour, whilst mercuric oxy-carbonate is dark red, it is thus possible to distinguish between soluble carbonates and hydrogen-carbonates.

FERROUS CARBONATE (SYN. *Carbonate of Iron*). **Formula, $FeCO_3$. Molecular Weight, 116.**

This compound occurs in nature as *spathic iron ore* and *clay iron-stone*. It may be obtained in a pure condition by precipitating a solution of ferrous sulphate with ammonium carbonate.

$$FeSO_4 + (NH_4)_2CO_3 = FeCO_3 + (NH_4)_2SO_4.$$

In order to prevent as much as possible the decomposition which takes place during the operation of drying, the B.P. separates the precipitate by filtration, partially dries it by pressure in calico, and then mixes it with sugar, by which means alteration is greatly retarded.

Ferri carbonas saccharata is met with in small coherent lumps, of a grey colour, with a sweet, very feeble, chalybeate taste. It dissolves with effervescence in warm hydrochloric acid diluted with half its volume of water, and is converted into ferric oxide by heating in the air.

(*For analysis and estimation, see Author's* **Analytical Chemistry**, *pages* 96 *and* 159.)

The highest (theoretically) attainable percentage is 46. In practice few samples contain the official proportion of carbonate. Out of twenty-five samples examined a few years ago, only one contained a trifle over the amount, and two others were within a single per cent. of the same. Not more than one out of three samples will contain 37 per cent., which is reckoned an average purity.

It is sometimes the practice to mix the ferrous sulphate with sugar before solution. To provide against the possibility of the action of dissolved air, it might be advisable to boil the ferrous sulphate with water for some time, and add a few drops of aqueous sulphurous acid, until the precipitate (if any) is entirely redissolved. If a few drops of sulphurous acid be also added to the tetr-ammonium carbonate solution, oxidation would still farther be prevented. In spite of these precautions, it is impossible to entirely arrest oxidation. But by washing with water which has been boiled until the ebullition has become irregular and convulsive, and using the utmost despatch in mixing with the sugar, a product of 45 per cent. may practically be obtained.

It oxidizes much more readily in moist than in dry air. The reddish brown powder which passed by the name of subcarbonate (or carbonate) of iron some years back, was that now known as ferric oxyhydrate. It results when ferrous carbonate is dried with free exposure to the air and without admixture of sugar. The advantage ferrous carbonate is believed to possess over and beyond ferric oxyhydrates and oxide is a more ready solubility in gastric juice. Ferrous carbonate is the active constituent of *mistura ferri composita*, the well known Griffith's mixture; and in consequence of the great rapidity of its oxidation when in solution, the ferrous sulphate is directed to be added at the last, and in crystals, the bottle being instantly corked. Practical pharmacists keep in readiness a concentrated emulsion with the omission of the iron, the ferrous sulphate and the requisite rosewater being added at the moment of dispensing. By this means an admirable result is gained.

BISMUTH OXY-CARBONATE (or **BISMUTHYL CARBONATE**) (SYNS. *Bismuthi Carbonas. Subcarbonate of Bismuth*). **Formulæ, $Bi_23CO_3.2Bi_2O_3$, or $(BiO)_2CO_3$**; *as in B.P.* **$Bi_2O_2CO_3$**.

This is the white precipitate produced by introducing a solution of bismuthous nitrate into a solution of tetr-ammonium carbonate, collecting the precipitate, washing and drying at a temperature not exceeding 150° F.

$$4Bi3NO_3 + 3N_4H_{16}C_3O_8 = 2(BiO)_2CO_3 + 12NH_4NO_3 + 7CO_2.$$

The bismuthyl carbonate contains one molecule of H_2O, which may be driven off by a heat of 212° F. In consequence of its containing this when allowed to dry spontaneously, the air-dried salt ought really to be represented by a much more complex formula than that given in the B.P. This complex form, however, need not be used in the equation, as its exact composition has not been definitely ascertained.

Bismuthi carbonas is a white powder, blackened by sulphuretted hydrogen; insoluble in water, but soluble with effervescence in nitric acid. Heated to redness, it turns yellow, forming bismuthous oxide.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 97.)

COMPOUNDS OF CARBON WITH THE HALOGENS

CARBON TETRACHLORIDE (SYN. *Tetrachloromethane*). **Formula, CCl_4.**

Is a colourless liquid boiling at 138.5° Fahr., and having a specific gravity of 1.50. It may be formed by the action of excess of chlorine on methane in direct sunshine; but it is more commonly prepared by passing chlorine and the vapour of carbon disulphide through a red hot tube. When the vapour of the tetrachloride is passed through a red hot tube, either by itself or mixed with hydrogen, a mobile liquid is obtained, having a gravity of 1.629, and boiling at 241° Fahr., which is **carbon dichloride**, or *tetrachlorethene*, C_2Cl_4.

It has been already seen, that when ethene is mixed with chlorine, ethene chloride, $C_2H_4Cl_2$, is formed; and if this oily liquid be then exposed to sunshine in contact with excess of chlorine, we obtain a white solid, crystalline and aromatic, insoluble in water, but soluble in alcohol and ether. This is the remaining chloride, viz., **carbon trichloride**, or *hexchlorethane*, C_2Cl_6.

CARBON TETRABROMIDE (SYN. *Tetrabromethane*). **Formula, CBr_4.**

CARBON TETRA-IODIDE (SYN. *Tetra-iodomethane*). " **, CI_4.**

Are both crystalline solid bodies, the former white and the latter red. The first produced by the action of bromine in the presence of antimonious bromide on carbon disulphide, and the second by heating carbon tetrachloride with aluminium iodide. Both form di- and tri- compounds analagous to the chlorides, but all solid.

All these compounds are really haloid ethers, which will be fully described further on.

CARBONYL CHLORIDE (SYNS. *Carbon Oxychloride. Phosgene Gas*). **Formula, $COCl_2$.**

This is a pungent, suffocating gas, decomposable by water, and therefore having to be collected over mercury. It is condensable to a liquid at 32° Fahr., and is produced when chlorine and carbonous oxide are exposed to sunshine, or, more practically, by passing carbonous oxide through antimonic chloride.

$$SbCl_5 + CO = COCl_2 + SbCl_3.$$

COMPOUNDS OF CARBON AND SULPHUR.

CARBON DISULPHIDE. Formula, CS_2. Molecular Weight, 76.

This highly important solvent in the arts is prepared by passing the vapour of sulphur over red-hot charcoal.

$$\underset{4\text{ vols.}}{C_2 + 2S_2} = \underset{4\text{ vols.}}{2CS_2}.$$

The crude product thus obtained has a very offensive odour, which was at one time considered natural, but has now been found to be owing to contamination with a variety of sulphur compounds. These are removed by agitation with mercuric chloride, or recently-reduced copper, and the purified product is then redistilled. As thus prepared it is a colourless mobile liquid, with a faint, but still somewhat disagreeable odour, boiling at 116° F., and having a specific gravity of 1·27. It cannot be solidified, and its evaporation *in vacuo* produces extreme cold. It dissolves iodine, sulphur, phosphorus, camphor, fixed and volatile oils, and caoutchouc. It is miscible with alcohol and ether, and burns in the air with a blue flame, producing sulphurous and carbonic anhydrides. Besides its solvent powers, it is a most powerful reducing and sulphurizing agent, converting metallic oxides into sulphides, and reducing nitric acid, dichromates, and permanganates. It is much employed in the extraction of oils and fats, and in the vulcanizing of india-rubber.

By exposing carbon disulphide to direct sunshine in sealed tubes for some time, a brown powder is deposited. This is **carbon monosulphide, CS**, which is destitute of smell, and has a specific gravity of 1·66, and inflames in contact with strong nitric acid.

CHAPTER IX.

BORON, SILICON, SELENIUM, AND TELLURIUM.

BORON. Symbol, B. Atomic Weight, 11.

Is a metalloid resembling carbon in many respects, and, like it, existing both in the crystalline and amorphous condition. Amorphous boron is a greenish grey powder, infusible, and burning with great rapidity in oxygen or in the air, to form boric anhydride; while crystalline boron is somewhat similar in appearance to the diamond. The former is prepared by fusing boric anhydride with potassium, and the latter by fusing the same body with aluminum.

Boron combines with oxygen to form **boric anhydride**, B_2O_3, which in turn produces boracic acid.

HYDROGEN BORATE (SYNS. **Boracic Acid.** *Orthoboric Acid*). **Formula, H_3BO_3. Molecular Weight, 62.**

Is prepared by making a strong solution of borax in boiling water, adding hydrochloric acid until an acid reaction is obtained, and cooling, when the boracic acid crystallizes out, and may be washed with cold water, and dissolved for use in rectified spirit. A solution of boracic acid so obtained is used in the B.P. as a test for the presence of turmeric in powdered rhubarb. When crystallized it is in colourless crystals, soluble in water and spirit, which when strongly heated lose water and become converted into a glacial mass of boric anhydride. Besides this acid we have a metaboric acid, HBO_2, forming metaborates; and a tetraboracic acid is also presumed to exist, $H_6B_4O_9$. Borates are frequently insoluble in water.

(*For detection and separation of Boracic Acid and Borates, see Author's* **Analytical Chemistry**, *page* 59.)

BORAX (SYNS. *Sodium Dimetaborate. Biborate of Soda. Tinkal*). **Empirical Formula, $Na_2B_4O_7 10H_2O$: Rational Formula $(NaBO_2)_2B_2O_3 10H_2O$.**

This peculiar salt, so useful in blowpipe analysis, is found native on the shores of saline lakes in Thibet, and was formerly much imported under the name of *tinkal*. A new source has also been discovered in South America; beds of native calcium borate having been found in Iquique, in the vicinity of the deposits of sodium nitrate. It is now, however, chiefly imported from some recently-discovered beds in California, or prepared from the native boric acid found in volcanic regions. In certain parts of Italy, notably near *Castel-Nuovo*, a great number of jets of steam rise from the earth. They are called *suffioni*, and in condensing form small lakes called *lagoni*, in which the boric acid collects. The exact manner in which a non-volatile acid gets into the

steam jets has not been definitely proved. Some suppose that it is mechanically carried up by the force of the jet, but the hypothesis of M. Dumas is probably much nearer the truth. He supposes that the boron exists in the jets as boron sulphide, and on coming into contact with watery vapour it is decomposed, thus :—

$$B_2S_3 + 6H_2O = 2H_3BO_3 + 3H_2S.$$

This is the more probable, seeing that the gas evolved from the *suffioni*, after contact with water, contains 4 per cent. of sulphuretted hydrogen. The process of obtaining boric acid and the subsequent production of borax consists in making artificial reservoirs or lakes round a series of *suffioni* on the side of a hill, all communicating by means of wooden tubes. Water is then pumped into the highest reservoir, and allowed to remain until by the action of the hot jet it is raised nearly to the boiling point, and impregnated with about 1 per cent. of boric acid. It is then allowed to run into the next reservoir, where it is acted upon by a fresh jet, and still further charged; until, by passing down the whole series of lakes, it becomes sufficiently concentrated. It is allowed to settle, and is finally evaporated to the crystallizing point in an immense flat vessel of lead, aided by the natural heat from the *suffioni*. The acid having been separated and dried, is re-dissolved in water, neutralized with a proper quantity of sodium carbonate, and the borax thus produced is purified by recrystallization. According to the temperature and degree of concentration two varieties of borax may be obtained, viz. :—

Prismatic Borax (official)	$Na_2B_4O_7 10H_2O$.
Octahedral Borax	$Na_2B_4O_7 5H_2O$.

The former is slightly efflorescent, and has a specific gravity of 1·7 ; while the latter absorbs moisture from the air, becoming opaque, and having a specific gravity of 1·8.

As to the official variety, the B.P. says that it should be met with in transparent colourless crystals, sometimes slightly effloresced, with a weak alkaline reaction ; insoluble in rectified spirit, soluble in water. A hot saturated solution, when acidulated with any of the mineral acids, lets fall, as it cools, a scaly crystalline deposit of boracic acid.

Borax is also soluble in glycerin, and such a solution (1 in 6 by weight) is official as *glycerinum boracis*.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 106.)

SILICON (SYN. *Silicium*). **Symbol, Si. Atomic Weight, 28.**

Is a metalloid closely resembling carbon, and like that element is allotropic, and capable of assuming a crystalline, a graphitoidal, and an amorphous state. It exists very extensively in nature as *sand* (hence its name, from *silex*). and may be isolated by the action of metallic potassium on potassium silicofluoride.

HYDROGEN SILICO-FLUORIDE (SYNS. *Hydro-fluosilicic Acid. Silico-fluoric Acid*). **Formula, H_2SiF_6.**

When hydrofluoric acid is brought into contact with sand, glass, or any similar silicium compound, **silicon fluoride** is produced. This is a gaseous body, colourless, and having a density of 3·6 referred to air. It is the forma-

ion of silicon fluoride which causes the powerful action possessed by hydrofluoric acid on glass:—

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

On heating together fluor-spar, powdered glass, and sulphuric acid, and passing the evolved silicon fluoride into water, it decomposes, depositing silicic anhydride, and leaving hydrogen silico-fluoride in solution:—

$$3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2.$$

As thus produced silico-fluoric acid is a fuming liquid which evaporates spontaneously at 100° F. When neutralized with sodium hydrate, it yields **sodium silico-fluoride** (Na_2SiF_6), which is often used as a test for potassium, as it produces with soluble salts of that metal, a transparent gelatinous precipitate, having the formula K_2SiF_6.

SILICIC ANHYDRIDE (SYNS. *Silica. Anhydrous Silicic Acid*). **Formula, SiO_2. Molecular Weight, 60.**

Exists in nature as *rock crystal*, *quartz*, *agate*, *opal*, *flint*, *sand*, and many other similar minerals. Rock crystal is nearly quite pure crystalline silica, and in the amorphous state it may be prepared by passing hydrogen silico-fluoride into water, as already shown. It is then a white tasteless powder, unalterable by ordinary sources of heat, but capable of fusion by the oxy-hydrogen flame. After ignition it is insoluble in water and all acids except hydrofluoric. It combines with water to form a series of hydrates which act as acids, the chief one being silicic acid, having the formula H_4SiO_4. These hydrates in turn produce a long series of silicates with metals, the formulæ of which are too complicated to be discussed in a work like the present. The great mass of minerals which come under the notice of the analyst contain silica in some form, and its detection and estimation is of importance. To effect this, the mineral is reduced to a very fine powder, and intimately rubbed with three times its weight of a mixture of potassium and sodium carbonates previously dried with care. The whole is introduced into a silver or platinum crucible, and heated until tranquil fusion sets in. After maintaining the heat for a short time, the crucible and its contents are cooled and placed in a basin with a little water and a slight excess of hydrochloric acid, and boiled. When the mass has detached itself from the crucible the latter is removed, and the whole contents of the basin are evaporated to dryness, and maintained for half an hour at a temperature of 280° to 300° F. By this treatment the silica is rendered anhydrous and absolutely insoluble, and it only remains to treat once more with very dilute hydrochloric acid, collect the insoluble silica on a filter, wash, dry, ignite, and weigh. On fusion with the mixture of carbonates as above described a potassium sodium silicate is formed which is soluble in water. On treating this solution with hydrochloric acid the silicic acid is set free, partly as a gelatinous precipitate, but a considerable portion remains dissolved. The evaporation to dryness, and subsequent heating, causes the decomposition of the silicic acid, which gives up water, and leaves the silica in an insoluble condition fit for collection.

Sodium Silicate is frequently prepared in the form of a strong solution which is known as *soluble glass* by fusing silica or sand with sodium carbonate and digesting in water, and is used for coating buildings, in order to prevent decay. It becomes totally insoluble by exposure to the air in contact with the stone, which is thereby covered by an impervious coating.

Sodium silicate is also used to adulterate soaps.

Glass is a mixture of noncrystalline and insoluble silicates of potassium,

sodium, calcium, magnesium, and lead, usually containing a large excess of silica. The following is the composition of some of the principal varieties of glass :—

Flint Glass . . .	Silica, Sodium Carbonate, and Plumbic Oxide.
Green Bottle Glass .	Silica, Sodium Carbonate, and Iron
Plate Glass	Silica, Potassium Carbonate, Calcium Oxide
Refractory Chemical Glass	Silica, Potassium Carbonate, Calcium and Magnesium Oxides, with traces of Aluminium and Manganese.

The materials, such as white sand, sodium carbonate, and red lead, are fused together in a crucible until perfectly bright and free from bubbles of escaping gas. The workman then dips in his tube, the article required is blown, and afterwards annealed by being allowed to cool gradually in an oven. Were this latter process not perfectly carried out, glass would not bear the slightest change in temperature without flying to pieces.

Porcelain and **stoneware** are essentially aluminium silicate : the former being very pure, and the latter containing iron, calcium, etc. Both are made by fashioning clay into the desired shape, and then baking in a furnace. The glaze is communicated by throwing into the fire sodium chloride, which volatilizes, and combines with the outer portion of the ware to form a glistening coating of sodium silicate.

[The difference between stoneware and porcelain appears to be this, that the vitreous change in the porcelain is carried farther than in stoneware, until it approaches a condition of glass; while earthenware contrasts with both materials in respect to its more or less porous body and dry fracture, also in being absorbent. (John Sparkes.)]

SELENIUM. Symbol, *Se*. Atomic Weight, 79·5. Atomicity, Dyad, Tetrad, or Hexad.

This element, discovered by Berzelius in 1817 among the refuse materials of a sulphuric acid factory, is interesting to medical men and pharmacists, from the fact of its being a not uncommon impurity in some varieties of commercial bismuth, to which it communicates dangerous properties, and cases have occurred where most unpleasant symptoms have followed the use of *Liquor Bismuthi* made from such samples. It is also found associated with sulphur in many ores, especially as a double selenide of copper and lead found in the Hartz Mountains. It is most easily prepared from the deposit found in the vitriol chambers of chemical works, where use is made of pyrites containing selenium. The deposit is treated with a mixture of nitric and sulphuric acids, and from this solution of selenious acid the selenium may be separated by diluting with four times its volume of water, and passing a current of sulphurous anhydride. The precipitate produced is taken up by agitating the liquid with carbon disulphide, and the selenium is finally recovered from the solvent by evaporation.

Like sulphur, selenium is *allotropic*, and is known both in the amorphous, vitreous, and crystalline states. In the amorphous condition it is in ductile red flakes, while in the vitreous state it is black and insoluble in carbon disulphide. The crystalline variety is prepared by heating the black modification to 204·8° F., and is bluish grey. Selenium fuses and boils below a red heat, giving a vapour having the odour of putrid horseradish. It burns in the air with a blue flame, forming SeO_2.

It forms with oxygen a series of acids as follows :—

Selenious Anhydride, SeO_2. Is produced when selenium is burnt in the

air or boiled with nitric acid. It is a white deliquescent solid, soluble in water to form selenious acid, H_2SeO_3. By passing any reducing gas, such as sulphurous anhydride or sulphuretted hydrogen, it is decomposed, yielding a red precipitate of amorphous selenium.

Selenic Acid, H_2SeO_4. Corresponds to sulphuric acid, but its anhydride has not been isolated. It is a syrupy liquid, evolving heat when mixed with water, and is prepared by passing sulphuretted hydrogen through plumbic selenate, which latter is formed by precipitating potassium selenate (produced by fusing selenium with nitre) with plumbic nitrate.

Selenium forms with hydrogen a compound, H_2Se, called seleniuretted hydrogen, similar to sulphuretted hydrogen, but much more offensive and dangerous.

Compounds of selenium exhibit the following reactions :—

I. Heated with sodium carbonate on charcoal in the blowpipe flame, they evolve a peculiar odour of decaying horseradish, and a red sublimate is produced on a piece of cold porcelain held close to the charcoal.

II. Soluble **selenites** yield a red precipitate of selenium with sulphurous acid, and a yellow mixture of sulphur and selenium with sulphuretted hydrogen supposed formerly to be a definite sulphide.

III. Soluble **selenates** give a white precipitate with barium chloride which is insoluble in dilute hydrochloric acid, but when heated with strong hydrochloric acid it dissolves, with evolution of chlorine.

TELLURIUM. Symbol, *Te*. Atomic Weight, 128.

Is a very rare element, also found on one occasion in an impurity in commercial bismuth. It was discovered by Muller in 1782, and is a pinkish white crystalline body, having a metallic appearance. Its compounds are very active irritant agents; and even the minutest trace existing by accident in *liquor bismuthi* imparts a horrible garlic odour to the breath. It burns in the air with a blue flame, yielding TeO_2, and dissolves in sulphuric acid to a purple red solution, from which it again separates on the addition of water. It forms the following series of oxides :—

Tellurous Oxide,	TeO_2,	forming	Tellurous	Acid,	H_2TeO_3
Telluric	TeO_3	„	Telluric	„	H_2TeO_4

Tellurous Oxide is found native as *tellurite*, and is fusible by heat, being a yellow glassy mass while hot, but changing to white on cooling. **Telluric Acid** is prepared like selenic acid, and when heated leaves **telluric oxide** as a yellow solid, insoluble in water and acids.

CHAPTER X.

NITROGEN.

NITROGEN (SYN. *Azote* [*French*]). **Symbol, N** *or* **Az** [*French*]. **Atomic Weight, 14. Density,** *referred to Hydrogen,* **14. Density,** *referred to Air,* **·972. Weight of a Litre, 1·254** *grammes* = **14** *criths.*

This body, which was discovered by Scheele and Rutherford in 1772, and called by the latter *mephitic air*, exists in the atmosphere, of which it constitutes four-fifths of the entire volume, the remaining fifth being oxygen, with a trace of carbonic anhydride, and some slight impurities. Ozone, the nature of which is still under investigation, must be included.

It is called by foreign chemists **azote**, because it does not support life (from the Greek ἀ [privative] not, ζωή, life); while by us it is named nitrogen, because it is the element which gives birth, as it were, to nitre.

Nitrogen is easily prepared, in a tolerably pure condition, by burning out the oxygen from an enclosed space of air by means of phosphorus. A piece of common phosphorus is wiped dry, and placed in a small porcelain capsule, which is floated on the surface of water contained in a flat dish. A light is then applied, and a glass bell-jar is quickly covered over the whole. The phosphorus commences to burn inside the jar, producing copious white fumes of **phosphoric anhydride** (P_2O_5) by uniting with the oxygen.

When all the oxygen has been consumed, the phosphorus ceases to burn, and the white fumes gradually disappear, because they dissolve in and combine with the water, to form **meta-phosphoric acid**; and thus eventually nothing is left in the jar but a colourless gas, which is almost pure nitrogen.

The steps of the process by which the oxygen is removed, may be thus represented :—

$$xN_2 + 2P_2 + 5O_2 = 2P_2O_5 + xN_2.$$
$$xN_2 + 2P_2O_5 + 2H_2O = 4HPO_3 + xN_2.$$

Nitrogen may also be isolated from the atmosphere by passing air slowly over red-hot copper, which absorbs the oxygen, and leaves the nitrogen; thus :—

$$Cu_2 + O_2 + xN_2 = 2CuO + xN_2.$$

Another way of proceeding, is that usually employed in the volumetric analysis of air. A quantity of air is introduced into a graduated tube inverted over a trough of mercury. The measure of air having been read off, a few drops of strong solution of potassium hydrate are introduced into the tube, which quickly absorb the carbonic acid gas. The volume is again read off, and a few drops of strong solution of pyrogallic acid are introduced, which combines with the potassium hydrate, forming potassium pyrogallate, a substance possessing an extraordinary power of absorbing oxygen.

When no further contraction of the gaseous contents of the tube is observable, the volume of pure nitrogen thus remaining is read off, and by a simple

calculation the respective volumes of the carbonic acid, oxygen, and nitrogen in the original volume of air are ascertained.

By this and similar methods of analysis the atmosphere has been proved to be constituted as follows:—

	By Weight.	By Volume.
Oxygen	23	20·8
Nitrogen	77	79·2
Carbonic Anhydride. / Aqueous Vapour / Ammonia Gas and organic impurities	traces	traces
	100	100·0

It is certain that the air we breathe is not a chemical compound, but simply a mechanical mixture, because the oxygen and nitrogen do not exist in their proper combining proportions, or in any fixed arithmetical relations to these proportions. Moreover, when the two are attempted to be combined in proportions to form air, neither contraction nor development of heat takes place in any marked degree; and indeed if the oxygen were not perfectly free, the air would not support the combustion of our fires* nor the respiration of animals.

To prepare nitrogen in a state of absolute purity, ammonium nitrite is heated in a retort. It is thus completely decomposed into water and free nitrogen.

The same result is obtained by heating together a mixture of potassium nitrite and ammonium chloride, thus:—

$$KNO_2 + NH_4Cl = N_2 + KCl + 2H_2O.$$

It may also be obtained by passing a current of chlorine through a solution of ammonium hydrate. When the latter is strong, each bubble of chlorine leaves the liquid with a flash of light. Great care must be taken that the point of neutralization of the hydrate is not approached, as nitrogen chloride (an extremely explosive liquid) might then be formed. The reaction is:—

$$8NH_4HO + 3Cl_2 = 6NH_4Cl + 8H_2O + N_2.$$

Pure nitrogen is a colourless, tasteless, and inodorous gas; entirely negative in all its properties; neither combustible nor a supporter of combustion or of life. Capable of condensation to a liquid by combined intense cold and great pressure, and practically insoluble in water. 100 gallons of water at 60° F. only dissolve about one gallon and a half of nitrogen. In combination nitrogen exhibits an atomicity equal to H_5, and is therefore truly a pentad; but in many cases part of the atomicity becomes latent, and it acts only as a triad. Examples may be seen in ammonium salts, and in ammonia gas. (*See* **Atomicity.**)

Nitrogen will not combine directly either with free oxygen or with free hydrogen, but will unite with the former when ozonized by the electric spark in presence of a strong alkali, and with the latter when presented in the nascent state.

With magnesium and boron it will combine at a red heat, and also with carbon heated to redness, in presence of an alkali, to form a cyanide of the alkali. (*See* **Cyanogen.**)

* If any one of the oxides of nitrogen were mixed with sufficient nitrogen for the mixture to have the percentage composition of air, the combination would not support combustion.

COMPOUND OF NITROGEN WITH HYDROGEN.

AMMONIA. Formula, NH_3. Molecular Weight, 17. Density, *referred to Air*, **·5890. Density,** *referred to Hydrogen*, **8·5. Weight of 1 Litre, ·7633** *gramme.*

Is a colourless gas, with a well-known pungent and irritating odour, which can be liquefied under a pressure of 6·5 atmospheres at a temperature of 62° Fahr., and even solidified by great cold and pressure. It is very soluble in water, which will absorb 700 times its own volume of the gas. It can be obtained, but with difficulty, by the direct combination of nitrogen and hydrogen, under the influence of a series of induction sparks produced by a powerful coil, and passing through the gaseous mixture from platinum-pointed wires :—

$$\underset{\text{2 vols.}}{N_2} + \underset{\text{6 vols.}}{3H_2} = \underset{\text{4 vols.}}{2NH_3}.$$

The molecule of ammonia gas therefore contains 1 volume N and 3 volumes H, condensing upon combination to 2 volumes. That is, 1 gallon of nitrogen and 3 gallons of hydrogen would produce 2 gallons only of NH_3.

Ammonia is practically produced :—

1. By the action of nascent hydrogen upon nitric acid or nitrates. This is seen when zinc, iron, tin, or cadmium are dissolved in very dilute nitric acid :—

$$4Zn + 9HNO_3 = 4Zn2NO_3 + NH_3 + 3H_2O.$$

Or better when a nitrate is acted on in solution by zinc or iron and dilute sulphuric acid.

2. By the action of zinc or aluminium and potassium or sodium hydrate upon a nitrate.

The metal and alkali first yield nascent hydrogen :—

$$8KHO + 4Zn = 4K_2ZnO_2 + 4H_2.$$

This acts upon the nitrate in presence of the water :—

$$KNO_3 + H_2O + 4H_2 = KHO + NH_3 + 3H_2O.$$

3. By the decomposition of nitrogenous organic matters.

(*a*) Such as cyanogen under the influence of water or alkalies.
(*b*) Such as albumen under the joint influence of oxidation and alkalies.

(*See Water Analysis in Author's* **Analytical Chemistry**, *page* 189.)

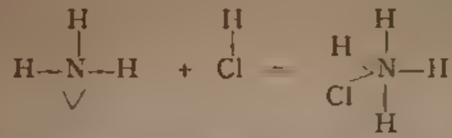
4. By heating ammonium chloride with calcium hydrate :—

$$2NH_4Cl + Ca2HO = CaCl_2 + 2NH_3 + 2H_2O.$$

A similar reaction will take place when any salt of ammonium is heated with an alkali.

Ammonia in uniting with water or acids (which it does with great avidity) not only displaces hydrogen, but unites with the hydrogen so displaced to form the basylous radical *ammonium* (NH_4). Nitrogen is truly a pentad in atomicity, but in ammonia two of the atomicities saturate each other, and so the nitrogen acts as a triad only. But it is always ready and eager to assume its proper state, and therefore when it is brought in contact with an acid it

does so, and is thus saturated to its full extent, when a salt of ammonium is produced:—



$$NH_3 + HCl = NH_4Cl.$$

This fact can be proved by simply holding near each other the stoppers from the hydrochloric acid and *liquor ammoniæ* bottles. Immediately this is done, a white smoke is formed, consisting of solid ammonium chloride produced by the combination of the two gases $NH_3 + HCl$.

Ammonia gas is very soluble in water, forming ammonium hydrate:—

$$NH_3 + H_2O = NH_4HO.$$

On passing a series of sparks through a known volume of ammonia in a tube over mercury, the volume gradually increases until it doubles itself, and then the result is found to be free hydrogen and nitrogen, in the proportion of 3 vols. H and 1 vol. N. A similar reaction may be caused by passing ammonia through a red-hot tube.

The hydrogen of ammonia may be displaced either by basylous or acidulous radicals, in the former case an **amine** is produced, and in the latter an **amide**. These compounds are of the greatest interest, and will be found fully described in a future chapter.

COMPOUNDS OF NITROGEN WITH OXYGEN.

With **oxygen** nitrogen forms five compounds in regular series, thus:—

Nitrous Oxide	N_2O.
Nitric Oxide	$N_2O_2 = 2NO$.
Nitrous Anhydride	N_2O_3.
Nitric Peroxide	$N_2O_4 = 2NO_2$.
Nitric Anhydride	N_2O_5

NITROUS OXIDE (Syns. *Laughing Gas. Nitrogen Mon-Oxide. Protoxide of Nitrogen*) **Formula, N_2O. Molecular Weight, 44. Density,** *referred to Hydrogen*, **22·06. Weight of a Litre, 1·98** *gramme*.

Prepared by simply heating **ammonium nitrate**, which is entirely decomposed into nitrous oxide and water:—

$$NH_4NO_3 = N_2O + 2H_2O.$$

The heat employed must be under 485° F.; but at first a temperature of 350° F. will cause decomposition.

The production of the gas is much facilitated by heating the crystals with a little water until perfect liquidity is effected, and then evaporating with constant stirring at a heat not exceeding 300° F. until the salt is converted into a fine white powder. Nitrogen mon-oxide may also be produced in a state of great purity by dissolving zinc in nitric acid largely diluted with water:—

$$2Zn_2 + 10HNO_3 = N_2O + 4Zn2NO_3 + 5H_2O.$$

In practice the zinc is shaken with 1 volume of nitric acid, 1 volume of sulphuric acid, and 50 volumes of water, the gas is purified by passing through concentrated sulphuric acid. When nitrous oxide is prepared from ammonium nitrate, the latter should first be tested for ammonium chloride, as, should

that substance be present, chlorine would be formed, which might cause fatal effects when administering the gas as an anæsthetic. Traces of higher oxides may be removed by ferrous sulphate, and any acidulous impurity by sodium or potassium hydrate. Nitrous oxide is a colourless gas, with a sweet taste, soluble to a considerable extent in water* (100 gallons would dissolve nearly 80 gallons of the gas at an ordinary temperature). It is capable of liquefaction under a pressure of 30 atmospheres, when cooled to the freezing point of water. Liquid nitrous oxide on evaporating produces such intense cold that it will partially freeze itself, and become a white snow-like substance.

The most important property of nitrous oxide is its power of producing when inhaled a kind of intoxication coupled with insensibility to pain: it is therefore much used in dentistry and minor surgical operations. It dissolves in the blood, which acquires for the time a peculiar tint; but with most persons its action is transient, and it does not leave any troublesome effects behind.

Many bodies which burn in oxygen, also burn with considerable brilliancy in this gas till all the oxygen has been removed. It will be found that after the experiment there will still remain a volume of free nitrogen equal to that of the nitrous oxide, proving that the volume of nitrogen required to form nitrous oxide is equal to the resulting oxide, viz., two volumes:—

$$\underset{\text{2 vols.}}{N_2O} = \underset{\text{2 vols.}}{N_2} + \underset{\text{1 vol.}}{O.}$$

The same fact may be proved by passing the gas through red-hot tubes, or exploding it with hydrogen, which forms water, and sets free nitrogen:—

$$\underset{\text{2 vols.}}{N_2O} + \underset{\text{2 vols.}}{H_2} = \underset{\text{2 vols.}}{N_2} + \underset{\text{2 vols.}}{H_2O.}$$

Mixed with oxygen or air, nitrous oxide will not form red fumes; but should it do so, it is then contaminated with the next compound, nitric oxide.

NITRIC OXIDE (SYNS. **Nitrosyl.** *Nitrogen Dioxide. Binoxide of Nitrogen. Deutoxide of Nitrogen. Azotyl*). **Formulæ,** N_2O_2, *or* **NO. Molecular Weight, 30. Density,** *referred to Hydrogen,* **15. Weight of 1 Litre, 1·344** *gramme.*

This gas is usually produced when nitric acid acts so as to dissolve a metal, or to raise a body from a lower to a higher state of oxidation, as for instance iron from the ferrous to the ferric state. (*See* **Ferric Chloride** *and* **Ferric Sulphate.**) Most commonly it is prepared from copper, since that metal dissolves easily in dilute nitric acid without the aid of heat, although it is usual to warm gently in order to quicken the action. The copper is placed in a flask, fitted with a funnel tube, extending to the bottom, and a delivery tube just passed through the cork. Sufficient water is added to nearly cover the copper, and half as much strong nitric acid is poured in by the funnel tube. At first the flask appears to be filled with red fumes, but soon the air becomes driven out, and a colourless gas is given off, which can be collected over water. This is the nitric oxide. It is a very dangerous gas to breathe, and should always be made in an open place or proper fume chamber. The moment it comes in contact with the air, it unites with the oxygen, and produces red fumes, which consist chiefly of nitric peroxide:—

$$\underset{\text{4 vols.}}{2NO} + \underset{\text{2 vols.}}{O_2} = \underset{\text{4 vols.}}{2NO_2.}$$

* A solution made under six or seven atmospheric pressures, is sometimes used as a stimulant.

When nitric oxide is passed over red-hot carbon, it is decomposed into carbonic anhydride and nitrogen :—

$$\underset{4 \text{ vols.}}{2NO} + C = \underset{2 \text{ vols.}}{CO_2} + \underset{2 \text{ vols.}}{N_2}.$$

When mixed with an equal volume of hydrogen, and a light or spark applied, combustion ensues, and water and free nitrogen are produced :—

$$\underset{4 \text{ vols.}}{2NO} + \underset{4 \text{ vols.}}{2H_2} = \underset{2 \text{ vols.}}{N_2} + 2H_2O.$$

When nitric oxide is mixed with sulphuretted hydrogen and passed over *soda lime*, it is converted into ammonia gas. When produced in presence of a ferrous salt, it is absorbed, and combines with the salt to produce a dark coloured compound, which is instantly decomposed by heat, and *slowly* by exposure to the air. It contains two molecules of the iron salt and one NO, the compound with ferrous sulphate having the formula $(FeSO_4)_2NO$.

Nitric oxide is insoluble in water, but has lately been liquefied by extreme cold and pressure. It can act as a monad radical, and replace hydrogen. This is a common occurrence in organic chemistry. When it so behaves it is called **nitrosyl.**

NITROUS ANHYDRIDE (SYNS. *Nitrous Acid. Nitrogen Trioxide*). **Formula, N_2O_3. Molecular Weight, 76.**

Is (at a temperature of 0° F.) a bluish liquid, emitting red fumes, prepared by mixing 4 vols. of nitric oxide and 1 vol. of oxygen together, in a glass tube surrounded by a strong freezing mixture capable of producing a temperature 20 degrees below the freezing point of water.

$$2NO + O = N_2O_3.$$

It is very unstable, and when brought into contact with water is decomposed into nitric acid and nitric oxide :

$$3N_2O_3 + H_2O = 2HNO_3 + 4NO.$$

In this case, therefore, practice does not bear out the theory, which would be that nitrous anhydride should combine with water to form nitrous acid, thus :—

$$N_2O_3 + H_2O = 2HNO_2.$$

But although we cannot really isolate and preserve pure nitrous acid, yet such an acid must exist, as there is a definite class of salts called **nitrites,** which have for their acidulous radical NO_2, behaving as a monad. An impure substance, called *nitrous acid*, is prepared by acting on starch or arsenious acid with nitric acid. The commercial nitrous acid thus prepared is a solution of nitrous anhydride in nitric acid, which is decomposed by dilution with water, in a similar manner to pure anhydride. The action of nitric acid upon arsenious acid may be thus shown :—

$$As_2O_3 + 2HNO_3 = As_2O_5 + N_2O_3 + H_2O.$$

AMMONIUM NITRITE (SYN. *Nitrite of Ammonia*). **Formula, NH_4NO_2.**

Already referred to under **nitrogen,** where its production is shown from ammonium chloride and potassium nitrite.

POTASSIUM NITRITE. Formula, KNO_2.

Prepared by heating **potassium nitrate** until **oxygen** ceases to be evolved, and then boiling out with alcohol, and crystallizing from the alcoholic solution.

ARGENTIC NITRITE (SYN. *Nitrite of Silver*). **Formula, $AgNO_2$.**

A white precipitate produced by potassium nitrite in a solution of argentic nitrate, and sometimes contained in fused argentic nitrate (*lunar caustic*), being formed by the heat employed.

When dried and ignited, it leaves a residue of pure metallic silver, and this reaction has been the means of proving the molecular weight of nitrous acid. 154 parts by weight of argentic nitrite yield 108 parts, or one atomic weight, of silver. The loss is therefore 46 parts of N and O, and substituting one part of hydrogen for the 108 of silver left, we have the molecular weight of nitrous acid fixed at 47, which agrees with the formula HNO_2.

CUPRIC NITRITE (SYN. *Nitrite of Copper*). **Formula, $Cu(NO_2)_2$.**

Forms a solution of a peculiar apple-green colour, which when once seen is almost unmistakable. When a mixture of aqueous solutions of cupric sulphate and plumbic nitrite (the result of heating lead with plumbic nitrate) is made, cupric nitrite is produced in solution, which is converted by the absorption of oxygen into cupric nitrate.

POTASSIUM COBALTOUS NITRITE. Formula, $(Co_2O)4NO_2,6KNO_2$.

A yellow crystalline precipitate, produced when excess of potassium nitrite is added to a solution of cobaltous chloride, slightly acidulated with acetic acid. Quite insoluble in cold, but soluble in hot water. This substance is important, as it serves as a means of separating cobalt from nickel.

Nitrites are also produced by the oxidation of ammonia gas, and often occur in the drinking waters of our cities and villages. Such water is looked upon with suspicion, as the nitrites might arise from oxidized sewage matter.

(*For detection of Nitrites, see Author's* **Analytical Chemistry**, *page* 61.)

NITRIC PEROXIDE (SYN. *Hyponitric Acid*). **Formula, $N_2O_4 = 2NO_2$.**

This oxide constitutes the chief portion of the red fumes formed when nitric oxide comes in contact with the air. It is also given off when plumbic nitrate is heated to redness :—

$$2Pb2NO_3 = 2PbO + 2N_2O_4 + O_2.$$

It can be condensed by great cold, first to a liquid and then to a solid state, while the oxygen passes off. It is also produced in the manufacture of *hydrargyri oxidum rubrum*, during the heating of the mercuric nitrate with metallic mercury in the last stage of the process :—

$$Hg2NO_3 + Hg = 2HgO + 2NO_2.$$

In combination with a little water, it forms both *nitrous* and *nitric* acids :—

$$2NO_2 + H_2O = HNO_3 + HNO_2.$$

With excess of water the nitrous acid is itself decomposed into nitric acid and nitric oxide.

In common with all the other oxides of nitrogen already studied, this body, although perfectly unaffected by a red heat, is decomposed into nitrogen and oxygen by the electric spark at 86° F., but the action is not perfect, owing to a partial recombination taking place.

In the same manner **nitrous oxide** is decomposed by the spark, two distinct actions taking place, thus :—

$$1.\ N_2O = N_2 + O.$$

$$2.\ 4N_2O = N_2O_4 + 3N_2.$$

With **nitric oxide** the spark quickly produces the following simultaneous **decompositions**:—

$$1.\ 2N_2O_2 = N_2O + N_2O_3.$$
$$2.\ 2N_2O_2 = N_2O_4 + N_2.$$

After a long continuance of sparks, the whole is decomposed into N_2 and O_2 with a little N_2O_4. These are the researches of M Berthelot, who also states that **nitrous oxide** supports flame more readily than nitric oxide, because at a red heat the former body entirely breaks up into its elements, while at the same temperature the latter body also produces nitric peroxide.

The group NO_2 is a monad radical, and, like NO, is capable of replacing hydrogen in many compounds It is called, when acting thus, *nitryl*, and an immense number of *substitution products* in organic chemistry are thus produced, such as nitrocellulose, nitrobenzene, and nitroglycerin, which are fully considered later on.

NITRIC ANHYDRIDE (SYN. *Anhydrous Nitric Acid*). **Formula, N_2O_5. Molecular Weight, 108.**

Prepared by decomposing perfectly dry argentic nitrate with chlorine gas, and collecting the brilliant white crystals which are formed, in a receiver immersed in a freezing mixture.

$$4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2.$$

It combines with water, causing a great evolution of heat and forming nitric acid. It melts at 86° F., and decomposes when heated to about 113° F. It cannot always be preserved, even at the ordinary temperature and in closed vessels Except after becoming moist, it possesses no acid properties; but it combines with water with great avidity, to form .—

HYDROGEN NITRATE (SYNS. **Nitric Acid.** *Spirits of Nitre. Aqua Fortis*). **Formula, HNO_3. Molecular Weight, 63.**

This acid is not found in the free state; but is always prepared by distilling sodium nitrate or potassium nitrate with sulphuric acid, thus:

$$NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4.$$
$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4.$$

Using this proportion of sulphuric acid with sodium nitrate, the action takes place freely at a low temperature, and sodium hydrogen sulphate is produced.

If a fresh portion of sodium nitrate be added, and the heat greatly raised, a second reaction will set in, and nitric acid will be again given off; the neutral sodium sulphate being produced:—

$$NaNO_3 + NaHSO_4 = HNO_3 + Na_2SO_4.$$

The latter process, however, tends to produce an acid containing nitric peroxide, owing to the high temperature required partially decomposing the nitric acid formed.

The B P. thus describes nitric acid.—

A colourless liquid, having a specific gravity of 1·42. When exposed to the air, it emits an acrid, corrosive vapour. If it be poured over copper, dense red vapours are immediately formed (nitric peroxide gas), but if the acid be mixed with an equal volume of water, and then added to the copper, it gives off a colourless gas (nitric oxide), which acquires an orange-red colour as it mixes with the air (nitric peroxide). The boiling-point of the acid is 250° F It contains 70 per cent. of HNO_3.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 101.)

The B.P. *acidum nitricum dilutum* is thus prepared :—

Dilute 6 fluid ounces of nitric acid with 24 fluid ounces of water, then add more water, so that at a temperature of 60° it shall measure 31 fluid ounces. The resulting dilute acid has a specific gravity of 1·101. It contains 17·44 per cent. of HNO_3.

It is possible to produce a fuming nitric acid much stronger than the B.P.

Absolute nitric acid has a specific gravity of 1·52. It is not commercially obtainable, the strongest being the 93 per cent. acid, which has the specific gravity, 1·5. The "single" *aqua fortis* contains from 30 to 35 per cent. of N_2O_5, and the "double strength" about 50 per cent. by weight.

It has been found that the B.P. acid, being a definite hydrate, having the true formula, $2HNO_3 + 3H_2O$, is much less liable to decomposition and the development of nitric peroxide by exposure to light, than the strong acids, besides being more certain and uniform in its action on metals.

For instance, iron is violently attacked by the B.P. acid of 1·42 specific gravity, indeed so violently that in making *liquor ferri pernitratis* we are specially warned to dilute the acid to moderate the action; and yet iron is not the least affected by immersion in fuming HNO_3 of 1·52 specific gravity, but exhibits what is called **passivity**, refusing even to dissolve when subsequently immersed in B.P. acid, until it has been touched by a metal strongly electro-negative, such as platinum. Even the B.P. acid acts unwillingly on silver and mercury, unless aided by dilution and a gentle heat. As regards the action of nitric acid on metals generally, it may be said that it dissolves them all with the exception of gold and platinum, on which it has no action; and tin and antimony, with which it forms insoluble compounds (stannic and antimonic oxides). Tin will, however, dissolve in very dilute cold nitric acid, as will also zinc and iron, with the production both of nitrous oxide and of ammonia, in greater or less quantity. The formation of ammonia from zinc and nitric acid may be thus represented :—

$$2Zn_2 + 9HNO_3 = 4Zn2NO_3 + 3H_2O + NH_3.$$

Nitric acid stains the skin yellow. This stain, the colour of which resembles that caused by iodine and bromine, can be readily distinguished from others by not altering when the part tinted is warmed, and being intensified into orange upon treatment with an alkaline hydrate. By the action of potassium permanganate the yellow stain is converted into a dark-brown colour. On dissolving this in a warm and weak solution of oxalic acid, or in sulphurous acid, which decomposes and decolorizes it with even greater facility, all traces of the yellow coloration will be found to have disappeared.

NITRO-HYDROCHLORIC ACID.

When nitric and hydrochloric acids are mixed together, they react on each other, producing free chlorine and nitrosyl chloride, thus :—

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

The liquid obtained in this manner is called *aqua regia*, and is used for dissolving metals, such as gold and platinum, which resist the action of all other acids. The *acidum nitro-hydrochloricum dilutum*, B.P., is prepared by mixing 3 fluid ounces of nitric acid, and 4 fluid ounces of hydrochloric acid, letting the mixture stand for 24 hours and then adding 25 ounces of distilled water.

It is a colourless acid liquid. Specific gravity, 1·07.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 101.)

The acid may be distinguished from the dilute nitric and hydrochloric acids of the B.P. by the following tests :—

It gives a precipitate with argentic nitrate insoluble in nitric acid, and at

the same time it will convert ferrous sulphate to the ferric state, and cause an immediate blue colour when added to a mixture of potassium iodide and starch paste. The dilute nitric acid, on the one hand, will not precipitate silver, while, on the other, the dilute hydrochloric acid will not liberate iodine, nor raise iron to the ferric state.

METALLIC NITRATES.

All nitrates are soluble in water, especially when slightly acidulated with nitric acid. The nitrates of the alkalies are only decomposed by a very high temperature; but most of the nitrates of the heavy metals, such as copper, mercury, and lead, when heated, are readily decomposed, leaving a residue of oxide. Argentic nitrate, however, when heated leaves metallic silver.

(*For detection of Nitrates, see Author's* **Analytical Chemistry**, *pages* 62, 63.)

AMMONIUM NITRATE (SYN. *Nitrate of Ammonia*). **Formula, NH_4NO_3. Molecular Weight, 80.**

Prepared by neutralizing nitric acid by ammonium carbonate, and crystallizing. It is used for making *laughing gas*, and is also employed in freezing mixtures, as it absorbs while dissolving an immense amount of heat, and so produces intense cold. Made from the official carbonate, the action is,—

$$N_4H_{16}C_3O_8 + 4HNO_3 = 4NH_4NO_3 + 3CO_2 + 2H_2O.$$

The B.P. orders the evaporation of the solution until crystals are obtained, and keeping these fused at a temperature not exceeding 320° until the vapour of water is no longer emitted.

Thus made, it is a white deliquescent salt, in confused crystalline masses, having a bitter acrid taste. Soluble in less than its own weight of water, and sparingly soluble in rectified spirit. It fuses at a temperature of 320° F., and at 350° to 450° it is entirely resolved into nitrous oxide gas, N_2O, and the vapour of water.

SODIUM NITRATE (SYNS. *Nitrate of Soda. Cubic Nitre. Chili Saltpetre*). **Formula, $NaNO_3$. Molecular Weight, 85.**

Is found native in immense quantities in Peru and Chili, and is purified from the chlorides and sulphates which it contains by recrystallization. It is deliquescent, and therefore unfit for the preparation of gunpowder. Its chief uses are for making potassium nitrate, for mixing with manures as a top dressing for land, and for making nitric acid. It is used in analysis as an oxidizing agent. A mixture of 4 parts of sodium nitrate and 1 part of sodium carbonate, when fused with the ores of chromium or manganese, converts them into soluble chromates or manganates; so enabling them to be easily estimated. The same mixture, fused with arsenious acid, converts it into sodium arseniate; with sulphides sulphates are formed, and indeed, it will act on any mineral capable of oxidation. The crystals are not perfect cubes.

POTASSIUM NITRATE (SYNS. *Nitre. Saltpetre. Nitrate of Potash*). **Formula, KNO_3. Molecular Weight, 101.**

Is found native in certain soils in India, in which it is doubtless produced by the oxidation of the nitrogenous portion of the decaying vegetable matters on the surface of the soil, such action being assisted by the powerful tropical

heat, coupled with the moisture present in the air. Native saltpetre is much contaminated with calcium nitrate, and is purified by dissolving in water and adding potassium carbonate. The calcium carbonate formed having been allowed to subside, the clear liquor is drawn off and crystallized.

Purified nitre is in white crystalline masses, or fragments of striated six-sided prisms, colourless, of a peculiar saline taste. Thrown on the fire, it deflagrates; heated, it fuses, gives off oxygen, and becomes potassium nitrite.

Nitre may also be prepared, on a large scale, by mixing sodium nitrate with potassium chloride, and crystallizing several times to purify the product:—

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

The nitre, being much less soluble than the sodium chloride, crystallizes out first, and is thus separated. In France and some continental countries, artificial nitre beds were formerly made by mixing and exposing to the air heaps of decaying vegetable matters and *lime*. The heaps were watered from time to time with urine, until a quantity of calcium nitrate had been formed, which was then treated with potassium carbonate, to produce nitre. The crystals found on the surface of B.P. *extracta* are of two kinds in general. If cubes, they are usually potassium chloride; but if needle-like, they probably consist of potassium nitrate.

Potassium nitrate is not very deliquescent, and can therefore be used for making gunpowder. This is a mixture of nitre, sulphur, and charcoal, in certain proportions.

As all true gases are transparent, the opaque smoke given off when gunpowder is exploded must contain a solid substance, which is believed to be potassium sulphate, K_2SO_4; and the gases also formed are carbonic anhydride (CO_2), nitrogen, carbonous oxide (CO), and occasionally a little sulphurous anhydride (SO_2). The nitre, sulphur, and charcoal vary in amount in different countries, and also according to the character desired in the gunpowder itself; but a useful quality may be produced by mixing together 80 parts of the first, $7\frac{1}{2}$ of the second, and $12\frac{1}{2}$ parts of the last. The residue after combustion usually consists of potassium sulphate and carbonate.

ARGENTIC NITRATE (SYNS. *Nitrate of Silver. Lunar Caustic. Lapis Infernalis*). **Formula, $AgNO_3$. Molecular Weight, 170.**

Is prepared by dissolving silver, by the aid of a gentle heat, in dilute nitric acid, evaporating, and crystallizing:—

$$3Ag_2 + 8HNO_3 = 6AgNO_3 + 2NO + 4H_2O.$$

It is usually met with in tabular crystals, the primary form of which is the right rhombic prism, soluble in distilled water and in rectified spirit. It is also made into cylindrical pencils for the purpose of a cautery.

A small fragment heated on charcoal with the blowpipe, first melts and then deflagrates, leaving behind a dull white metallic coating (metallic silver).

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 101.)

As commercial silver (such as would be at hand to make nitrate) contains copper, it is necessary to know how to separate the one from the other. This may be done in a variety of ways.

1. The silver coin, or other alloy, may be dissolved in nitric acid, and the silver precipitated as chloride with sodium chloride. The precipitate, having been allowed to subside, is washed free from the copper by boiling with water, and decantation. It is then reduced to metallic silver, which is once more to be dissolved in dilute nitric acid, and crystallized. The reduction of the chloride may be effected,—

(*a*) By acidulating with sulphuric acid, and stirring with a zinc rod free from lead.

(*b*) By fusing in a crucible with a mixture of potassium and sodium carbonate.

2. The coin may be dissolved in nitric acid, the green solution thus obtained evaporated to dryness, and heated over the flame until red fumes cease to be evolved. By this means the more readily decomposed cupric nitrate is converted into insoluble oxide, while the argentic nitrate is left undecomposed.

A very common adulteration of argentic nitrate is potassium nitrate, which is added during crystallization This, if anything, increases the brilliant appearance of the crystals, and cannot be detected by the eye.

If a solution be made with distilled water, and all the silver having been precipitated by hydrochloric acid, and filtered out, the filtrate be evaporated to dryness, a residue will remain if nitre was present, which cannot occur with pure argentic nitrate. It is easy to prove the residue to contain potassium by qualitative analysis.

Solution of argentic nitrate is useful for detecting the following :—

Hydrates,	precipitate,	brown	Ag_2O.
Chromates,	do.	red . . .	Ag_2CrO_4.
Phosphates,	do.	yellow . . .	Ag_3PO_4.
Arsenites,	do.	yellow . . .	Ag_3AsO_3.
Arseniates,	do.	reddish . .	Ag_3AsO_4.
Chlorides,	do.	curdy white .	AgCl.
Bromides,	do.	dirty curdy white .	AgBr.
Iodides,	do.	curdy yellow . .	AgI.
Cyanides,	do.	curdy white . .	AgCy.
Ferrocyanides,	do.	white	Ag_4FeCy_6.
Ferricyanides,	do.	orange red	$Ag_6Fe_2Cy_{12}$.

Solution of argentic nitrate is therefore used extensively in the estimation of several of these radicals.

(*See Volumetric Analysis in Author's* **Analytical Chemistry**.)

ARGENT-AMMONIUM NITRATE (SYN. *Ammonio Nitrate of Silver*). **Formulæ, $2NH_4(NH_2Ag)_22NO_3$, *or* $2NH_3.AgNO_3$.**

When a strong solution of argentic nitrate saturated with ammonium hydrate, and perfectly clear, undergoes spontaneous evaporation, this compound is obtained in the form of crystals. It is useful in analysis for producing precipitates with free arsenious and phosphoric acids, which, otherwise, would not give rise to their neutral argentic salts in the presence of the nitric acid which would be formed from ordinary argentic nitrate. The usual reagent, employed as *ammonio nitrate of silver*, is prepared by adding very dilute solution of ammonium hydrate to a strong solution of argentic nitrate, until the precipitate at first produced is *nearly* redissolved, and then filtering.

CALCIUM NITRATE (SYNS. *Nitrate of Lime. Baldwin's Phosphorus*). **Formula, $Ca2NO_3$.**

Is used in the preparation of potassium nitrate. It occurs as a white or greyish efflorescence in caverns formed in calcareous rocks. The destruction of the plaster and necessity for frequent renewal of the whitewash upon the inner side of walls, is due to the formation of this highly deliquescent salt. If it be desired in a pure state, the most advisable method to obtain it, is to

dissolve calcium oxide, hydrate, or carbonate in nitric acid. It can b procured in crystals by careful evaporation, and exposing the concentrate solution to a current of dry air. Heat causes these crystals to fuse, an finally to become a dry powder, which, after being raised to low redness an exposed to light for a short time, is luminous in the dark; hence it receive its second synonym, from the name of its discoverer (Baldwin) and the wor phosphorus (a light-bearer). By a long-continued high temperature it i totally decomposed into calcium oxide.

STRONTIUM NITRATE (SYN. *Nitrate of Strontia*). **Formula, $Sr2NO_3$.**

May be procured from strontium sulphide (or the native carbonate *strontianite*) by solution in nitric acid. It is only employed in pyrotechny and (rarely) for producing the oxide. For the former purpose it mus be rendered perfectly dry, as it is naturally a deliquescent salt. It is wel adapted for exhibiting the flame reactions of the metal, being easily volatilize in contact with deoxidants at a high temperature.

BARIUM NITRATE (SYN. *Nitrate of Baryta*). **Formula, $Ba2NO_3$.**

Prepared by dissolving barium carbonate in nitric acid largely diluted with water, and crystallizing. This salt is used, instead of barium chloride, as a reagent for precipitating sulphuric acid when in the presence of silver or nitric acid. It is comparatively slightly soluble in water.

CUPRIC NITRATE (SYN. *Nitrate of Copper*). **Formula, $Cu2NO_3$.**

Obtained by dissolving copper or its oxide in dilute nitric acid. It crystallizes in pale blue prisms, having amounts of water of crystallization varying from $3H_2O$ to $6H_2O$, according to the temperature at which it is crystallized. It is decomposed by heat, leaving cupric oxide.

MERCUROUS NITRATE. Formula, $Hg_22NO_3.H_2O$.

Prepared by digesting excess of mercury with cold dilute nitric acid. It crystallizes in colourless, efflorescent, crystalline plates. It is not perfectly soluble in water, owing to its tendency to form basic salts; but a drop of nitric acid added ensures a clear solution. It is used in analysis, as being the only common soluble salt of mercury in the *mercurous* state. When heated it gives off NO_2, and leaves *hydrargyri oxidum rubrum*, HgO.

It is not in the B.P., but is produced in making the red oxide. (*See* **Mercuric Oxide.**)

MERCURIC NITRATE. Formula, $Hg2NO_3$. Molecular Weight, 324.

Prepared by dissolving mercury in nitric acid of about half B.P. strength.

$$3Hg + 8HNO_3 = 3Hg2NO_3 + 2NO + 4H_2O.$$

The solution is effected in the cold, but it is afterwards boiled to expel the excess of nitric oxide, and to ensure the formation of mercuric nitrate.

Liquor hydrargyri nitratis is a colourless and strongly acid solution of mercuric nitrate. Specific gravity, 2·246.

(*For analysis, see Author's* **Analytical Chemistry,** *page* 102.)

Unguentum hydrargyri nitratis also contains mercuric nitrate, being formed by causing lard and olive oil to be heated with a strongly acid solution of that salt till the whole froths up.

The frothing is caused by the liberation of carbonous and nitric oxides owing to the action of the NO_2 on the oleine of the fats, a portion of which is changed to *elaidine*, a fat isomeric with oleine, though differing in its properties. A red oil is formed at the same time, which colours the ointment; and it is a question whether a basic nitrate of a yellow colour, and having the formula $Hg_6O_4.4NO_3$, be not frequently produced if the acid evaporate too rapidly, although a large excess of acid is purposely used to prevent reduction as much as possible. Steel knives should never be used with this ointment.

There are several bodies which are regarded as mercuric oxynitrates. The mercuric tri-oxynitrate has the formula, $Hg_2N_2O_7$ or $Hg_6N_6O_{21}$, which may be written $(Hg_2O)_3 6NO_3$ or $3HgO.3Hg(NO_3)_2$. The mercuric tetr-oxynitrate is found to possess the empirical composition, $Hg_3N_2O_8$ or $Hg_6N_4O_{16}$, which is rationally regarded as $4HgO.2Hg(NO_3)_2$. The salt approximating most to the pure oxide is hexa-mercuric oxynitrate, $Hg_6N_2O_{11}$, otherwise $5HgO.Hg(NO_3)_2$.

All three may be readily obtained from mercuric nitrate: the first by evaporating a solution of that body rapidly; the second results from agitating the salt obtained with cold water, and the third by boiling the last mentioned product with water. Mercuric tri-oxynitrate, which may also be termed in accordance with its first formula di-mercuric oxynitrate, may be procured in white crystals, which are sometimes transparent, but readily become opaque. Mercuric tetr-oxynitrate (tri-mercuric oxynitrate) is a yellow powder, and hexa-mercuric oxynitrate is "brick-red" in colour. These formulæ may be remembered with ease (if the simplest are supposed to be correct), by the fact that the first contains one molecule, the second two, and the third five molecules of mercuric oxide united to one of mercuric nitrate.

FERRIC NITRATE (SYNS. *Pernitrate of Iron. Nitrate of Iron. Nitrate of Peroxide of Iron*). **Formula, Fe_26NO_3.**

This body is readily produced by the solution of metallic iron in diluted nitric acid, the reaction being:—

$$Fe_2 + 8HNO_3 = Fe_26NO_3 + 2NO + 4H_2O.$$

Liquor Ferri Pernitratis, B.P., is a clear reddish-brown solution, having a specific gravity of 1·107. It is made by simply steeping iron wire in very dilute cold nitric acid until dissolved. The object of using the acid cold, is to avoid fumes during the operation.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 102.)

Ferric nitrate may also be prepared by acting upon ferric oxide (or hydrate) with nitric acid. It may be obtained in crystals, which are sometimes almost pure white, but at other times possess a bluish tint, by adding strong nitric acid to a concentrated solution of the salt. By rapidly evaporating watery ferric nitrate, a basic or oxy-salt is formed, and the same result takes place when ferric hydrate is added. The oxynitrates are soluble in water.

COBALTOUS NITRATE (SYN. *Nitrate of Cobalt*). **Formula, $Co2NO_3$.**

Is readily formed from the hydrate or oxide by solution in nitric acid. It is commonly employed as an ink termed *sympathetic*, which, from being pale pink and almost invisible when cold, becomes a deep blue on warming. It is valuable in analysis as a blowpipe test, as it imparts a strong blue colour to aluminium oxide when a very small quantity is placed upon a solid suspected to contain aluminium, and heated before the blowpipe. It also tints zinc

oxide under similar circumstances, but in this case the colour is green. If a blowpipe bead of **borax**, or *microcosmic salt*, be moistened with this (or any other cobalt salt), it yields on reheating a clear, blue, glassy substance.

BISMUTHOUS NITRATE (SYN. *Nitrate of Bismuth*). **Formula, $Bi3NO_3$.**

Prepared by dissolving bismuth in slightly diluted nitric acid by the aid of heat :—

$$Bi_2 + 8HNO_3 = 2Bi3NO_3 + 2NO + 4H_2O$$

When the solution thus obtained is poured into water, a precipitate of bismuthous oxynitrate is produced.

BISMUTHOUS OXYNITRATE (SYNS. *Bismuthyl Nitrate. Bismuthi Subnitras*). **Formula, $BiONO_3H_2O$.**

Prepared by pouring a solution of **bismuthous nitrate** into **water.**

$$Bi3NO_3 + H_2O = BiONO_3 + 2HNO_3.$$

In practice, however, the nitrate is not completely decomposed, a portion remaining dissolved by the nitric acid produced :—

$$5Bi3NO_3 + 8H_2O = 4(BiONO_3H_2O) + Bi3NO_3 + 8HNO_3.$$

The B P. *bismuthi subnitras* is a heavy white powder in minute crystalline scales, blackened by sulphuretted hydrogen (forming bismuthous sulphide), insoluble in water, but soluble in nitric acid mixed with half its volume of distilled water, forming a solution which, poured into water, gives a white precipitate (characteristic precipitate of $BiONO_3$). It is turned yellow by heat or by boiling with an alkaline hydrate, being converted into the oxide.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 102.)

As even the so-called purified metallic bismuth often contains arsenic, it is advisable to get rid of that dangerous body. This is done by crystallizing the nitrate, and using the crystals only for making oxynitrate. When the bismuth is dissolved in nitric acid, the arsenic contained in it is changed into arsenic acid, which, being very soluble, remains in solution when the bismuthous nitrate is crystallized out. This is the usual commercial process, as only the exact quantity of water requires to be added, and so much filtration, &c., is saved.

Theoretically, bismuthous oxynitrate is viewed as being a nitrate of the monad basylous radical bismuthyl, BiO.

PLUMBIC NITRATE (SYNS. *Nitrate of Lead. Plumbi Nitras*). **Formula, $Pb2NO_3$.**

May be prepared :—

1. By dissolving litharge in dilute nitric acid.

$$PbO + 2HNO_3 = Pb2NO_3 + H_2O.$$

2. By boiling red lead with dilute nitric acid, filtering, and crystallizing.

$$Pb_3O_4 + 4HNO_3 = 2Pb2NO_3 + PbO_2 + 2H_2O.$$

3. By dissolving lead in dilute nitric acid by the aid of heat.

$$Pb_3 + 8HNO_3 = 3Pb2NO_3 + 2NO + 4H_2O.$$

It is met with in colourless octahedral crystals, which are nearly opaque, permanent in the air, of a sweetish astringent taste, and soluble both in water and alcohol. Heated, it evolves N_2O_4, and leaves plumbic oxide.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 103.)

COMPOUNDS OF NITROGEN WITH THE HALOGENS.

NITROGEN CHLORIDE (Syn. *Chloride of Nitrogen*). **Formula, NCl_3**

Obtained by the action of an excess of chlorine upon ammonia gas, or ammonium hydrate, or an ammoniacal salt. Also by the action of the last-named upon hypochlorous acid.

$$4NH_4HO + 3Cl_2 = NCl_3 + 3NH_4Cl + 4H_2O.$$

In the last case, the action would be :—

$$NH_4Cl + 3HClO = NCl_3 + HCl + 3H_2O.$$

Nitrogen chloride is a fearfully explosive, oily, yellow liquid, which must be prepared in a small leaden cup, and with every part of the apparatus perfectly free from grease. It has a peculiar sharp odour, is volatile, and is instantly decomposed by turpentine, phosphorus, and oily bodies, also by heat. If exploded in an iron or glass vessel, it reduces it to fragments.

NITROGEN BROMIDE. Formula, NBr_3.

Formed from **nitrogen chloride** and **potassium bromide**. Is a thick, reddish-brown, very volatile liquid, resembling the chloride as regards odour, and readiness of decomposition with phosphorus; and, like that body, being only of theoretical interest.

NITROGEN IODIDE. Formula, NI_3.

Is produced when finely-powdered iodine is dropped into ammonium hydrate. A brown liquid is produced, consisting of a solution of iodine in hydrogen iodide, and the nitrogen iodide is deposited as a black powder, which, when dry, explodes violently even when touched by a feather, and often without apparent cause. The real composition of this powder has been variously stated to be NHI_2 and NHI_3NH_3; but it is probably not a constant compound, which accounts for the conflicting analyses which have been given.

COMPOUNDS OF NITROGEN WITH CARBON.

Many of these are exceedingly complicated, and will be treated of hereafter; but the following are to be studied at this stage :—

CYANOGEN. Formula, *in the free state*, **$(CN)_2$. Molecular Weight,** *in the free state*, **52. Density,** *referred to Hydrogen*, **25·5. Density,** *referred to Air*, **1·81.**

A chemico-historical interest attaches to cyanogen, as it was the first compound radical whose existence was definitely ascertained. Its isolation was due to Gay Lussac, about thirty years after Scheele's original discovery in 1782.

It is a colourless gas, with a decided odour similar to that of bitter almonds. It can be liquefied by a pressure of 3·6 atmospheres at 45° F., and can be solidified by a temperature of 90 degrees below 0° F. It burns with a *peach blossom coloured flame*, producing nitrogen and carbonic anhydride, thus :—

$$\underset{2\ \text{vols.}}{(CN)_2} + \underset{4\ \text{vols.}}{2O_2} = \underset{4\ \text{vols.}}{2CO_2} + \underset{2\ \text{vols.}}{N_2}.$$

That is, one gallon of cyanogen mixed with two gallons of oxygen, and exploded, would yield two gallons of CO_2 and one gallon of nitrogen.

It is prepared by heating mercuric or argentic cyanide. These substances are decomposed by heat, evolving cyanogen, and leaving the metal, which, in the case of mercury, sublimes with a little unaltered cyanide :—

$$2Hg(CN)_2 = Hg_2 + 2(CN)_2.$$

Cyanogen, although truly CN, is usually represented by the symbol Cy, because it behaves in every respect like an element, and to use such a symbol saves complication of the formula. For instance, it is easier to write Cy_6, and remember that it stands for 6 times CN, than to write always C_6N_6. In future, therefore, Cy will stand for CN.

METALLIC CYANIDES.

HYDROGEN CYANIDE (SYNS. **Hydrocyanic Acid.** *Prussic Acid*). **Formula, HCy Molecular Weight, 27.**

Exists ready formed in the juice of the bitter *cassava*, and is also formed when bitter almonds are rubbed with water, and when the leaves of the *Prunus laurocerasus* are distilled with water. It may be simply prepared by mixing a solution of potassium cyanide with a slight excess of tartaric acid, when potassium acid tartrate deposits, and hydrocyanic acid remains in solution :—

$$KCy + H_2C_4H_4O_6 = HCy + KHC_4H_4O_6.$$

Procured in this way, the acid is not quite pure ; but the process is useful to the pharmacist on an emergency, as yielding in a few minutes an acid of nearly the requisite strength. This may be extemporized by using 100 grains of tartaric acid, 44 grains of potassium cyanide, and 2 fluid ounces of water. Shake violently, set aside to settle, and then draw off the clear liquid. The proper B.P. way of preparing the acid is, by distilling potassium ferrocyanide with sulphuric acid very largely diluted with water. The action is as follows (x representing an indefinitely large quantity of water) :—*

$$2K_4FeCy_6 + 6H_2SO_4 + xH_2O = 6HCy + 6KHSO_4 + K_2Fe_2Cy_6 + xH_2O.$$

It is important that the acid should be very dilute, because tolerably strong sulphuric acid will entirely decompose potassium ferrocyanide, forming ferrous, potassium, and ammonium sulphates (the latter from the nitrogen of the CN), and evolving carbonous oxide, thus :—

$$K_4FeCy_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

To practically make the B.P. *acidum hydrocyanicum dilutum*, place 2½ ounces of potassium ferrocyanide, dissolved in 14 ounces of water and acidulated with an ounce of sulphuric acid, into a retort connected with a well-cooled condenser, the beak of which dips under the surface of 8 ounces of water placed in a receiver, also kept cool. Distil the whole slowly, until 17 ounces in all have collected in the receiver. Lastly, dilute the acid thus produced until it shows a strength of 2 per cent. of real HCN, *i.e.* until 100 grains (110 minims) of it precipitated with excess of argentic nitrate, and the precipitate collected, washed, dried, and weighed, shall show ten grains of dry argentic cyanide ; or until 270 grains of it, rendered alkaline by the addition of solution of sodium hydrate, require 1000 grain-measures of the volumetric solution of argentic nitrate to be added before a permanent precipitate begins to form.

(*See Author's* **Analytical Chemistry**, *page* 156.)

* The substance $K_2Fe_2Cy_6$ is a double ferrocyanide of iron and potassium, called, after its discoverer, *Everitt's* salt. (*See* **Ferrocyanides.**)

Thus made, the acid is a colourless liquid with a peculiar odour. Specific gravity 0·997. It only slightly and transiently reddens litmus paper. Treated with a minute quantity of a mixed solution of ferrous and ferric sulphates, afterwards with potassium hydrate, and finally acidulated with hydrochloric acid, it forms Prussian blue.

Scheele's prussic acid is stronger than the B.P., and contains 5 per cent. real hydrogen cyanide.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 103.)

Hydrocyanic acid decomposes slowly when kept in the dark, but very rapidly in the light. In the case of the dilute acid of the B.P., this decomposition is attended with the formation of ammonium formate:—

$$HCN + 2H_2O = NH_4CHO_2;$$

a deposit of a peculiar brown substance being thrown down at the same time.

Pure hydrogen cyanide is prepared by passing chlorine over dry mercuric cyanide. It is a colourless and volatile liquid, boiling at 79° Fahr., and solidifying when cooled to 0° Fahr. It dissolves in water and alcohol in all proportions. In a state of vapour it yields, when exploded with excess of oxygen, carbonic anhydride, nitrogen, and water, thus:—

$$\underset{4\text{ vols.}}{2HCN} + \underset{5\text{ vols.}}{5O} = \underset{4\text{ vols.}}{2CO_2} + H_2O + \underset{2\text{ vols.}}{N_2}.$$

Or, reducing the whole to the simplest ratio, 2 gallons of vapour require $2\frac{1}{2}$ gallons of oxygen, and yield 2 gallons CO_2 + 1 gallon nitrogen. The remaining half-gallon of oxygen forming water with the hydrogen of the acid. By the action of hydrochloric or sulphuric acid, hydrocyanic acid is decomposed into formic acid and ammonia, but minute traces of either of them tend to preserve the dilute acid from decomposition. On the other hand, by heating ammonium formate to 392° Fahr., we obtain hydrocyanic acid and water.

Cyanogen combines with metals to form cyanides, of which it is the acidulous radical, acting as a monad.

Cyanides give reactions similar to hydrocyanic acid. They are all decomposed by heating with water. In the case of alkaline cyanides, ammonia and formate of the alkalies are produced:—

$$KCN + 2H_2O = KCHO_2 + NH_3.$$

But with those of heavy metals, carbonic anhydride, carbonous oxide, and ammonia are given off, and the metal is deposited with a little carbon. Alkaline cyanides heated in the air first yield cyanates:—

$$KCN + O = KCNO,$$

and then give off nitrogen and carbonic anhydride, leaving carbonates of the alkali:—

$$2KCNO + O_3 = K_2CO_3 + N_2 + CO_2.$$

(*For detection of Hydrocyanic Acid and separation of Cyanides, see Author's* **Analytical Chemistry**, *pages* 63, 64, *and* 65.)

An immense number of cyanides of organic basylous radicals exist, and they are a most interesting class of bodies. At present, however, we will only touch on a few metallic cyanides, merely noting that the organic salts above referred to are sometimes called *azoparaffins*, or *nitrils*, being viewed in the former case as compounds derived from hydrocarbons by the displacement of three atoms of hydrogen by one of nitrogen, or in the latter as compounds of nitrogen with triad radicals. Thus, hydrogen cyanide, HCN, may be called:—

	Azomethane	CHN (from methane CH_4).
or	Methenyl Nitril	$(CH)'''N'''$; from the triad Methenyl $(CH)'''$.

POTASSIUM CYANIDE. Formula, KCN = KCy.

Prepared,—

1. directly by synthesis, by passing nitrogen over a mixture of potassium hydrate and charcoal heated to redness.

2. By heating potassium ferrocyanide to redness in a closed vessel, forming a carbide of iron, and evolving nitrogen :—

$$K_4FeC_6N_6 \text{ or } K_4FeCy_6 = 4KCy + FeC_2 + N_2.$$

3. By fusing potassium ferrocyanide with potassium carbonate, forming potassium cyanate and iron, evolving carbonic anhydride :—

$$2K_4FeCy_6 + 2K_2CO_3 = 10KCy + 2KCyO + Fe_2 + 2CO_2.$$

This is the commercial process, and yields a sufficiently pure product for the purposes to which this salt is applied in the arts. Potassium cyanide is usually seen in opaque, white, broken, flat lumps It is alkaline to test paper, very poisonous, and smells strongly of prussic acid. It is commonly very deliquescent, and is used in photography for dissolving the unaltered argentic iodide or bromide from the plates, and so *fixing* the portrait by removing all substances capable of being acted upon by light.

MERCURIC CYANIDE. Formula, $HgCy_2$.

Is prepared by boiling potassium ferrocyanide with mercuric sulphate, and filtering hot. The salt crystallizes from this solution in white prisms resembling mercuric chloride in appearance, and is soluble in water and alcohol. Its solution is not precipitable by alkalies.

ARGENTIC CYANIDE. Formula, AgCy.

Is precipitated when argentic nitrate is added to hydrocyanic acid. It is a curdy-white substance, readily blackened by exposure to the light, and soluble both in ammonium hydrate and in strong boiling nitric acid. In presence of an excess of potassium or sodium hydrate it is converted into a soluble double cyanide, which explains the fact, that, in the volumetric test for the strength of hydrocyanic acid above mentioned, when the silver solution is first added to the cyanide, no precipitate is produced, owing to the formation of a soluble double cyanide of silver and sodium :—

$$2NaCy + AgNO_3 = AgCy.NaCy + NaNO_3.$$

On continuing to add the silver, a time arrives when, the double compound having been fully formed, it is in turn decomposed by excess of silver, and a white cloud of argentic cyanide is produced :—

$$AgCy.NaCy + AgNO_3 = 2AgCy + NaNO_3.$$

At the moment, therefore, when the precipitate appears, sufficient silver has been added to combine with *one half of the cyanogen present in the sample*, as is shown by the formula, AgCy.NaCy.

This reaction is taken advantage of to determine volumetrically the strength of a sample of hydrocyanic acid.

(*See Author's* **Analytical Chemistry**, *page* 156.)

The other cyanides are not of pharmaceutical importance.

Besides the simple cyanides, the radical **cyanogen** has a great tendency to form double salts, containing two metals, and not only so, but to combine with a portion of the heavy metal, and form a new radical, itself capable of

uniting with hydrogen to form an acid, which can in its turn produce salts. Thus, ferrous cyanide and potassium hydrate yield potassium ferrocyanide :—

$$3FeCy_2 + 4KHO = K_4FeCy_6 + 2Fe2HO.$$

Here part of the Fe combines with the cyanogen to form a new acidulous radical called **ferrocyanogen**, $FeCy_6$, which acts as a tetrad, and unites with four atoms of the monad potassium to form a definite salt (potassium ferrocyanide).

METALLIC FERROCYANIDES.

HYDROGEN FERROCYANIDE (Syn. **Hydro-Ferrocyanic Acid**).
Formula, H_4FeCy_6.

Prepared by mixing potassium ferrocyanide with an acid, such as hydrochloric or tartaric. As thus produced, in solution, it rapidly decomposes in contact with the air, forming hydrocyanic acid and Prussian blue.

POTASSIUM FERROCYANIDE (Syn. *Yellow Prussiate of Potash*).
Formula, K_4FeCy_6 $K_4FeC_6N_6$.

This salt, *which is not poisonous*, is prepared on the industrial scale by fusing hoofs, horns, hair, and other nitrogenous organic matters, in a closed iron pot with potassium carbonate and iron filings. The action is one of pure synthesis, *i.e.* these nitrogenous bodies produce the nitrogen and carbon, which combine with the potassium and form potassium cyanide. On treating the mass with hot water the cyanide is attacked by the oxide or sulphide of iron (the latter produced from the reduction of the sulphates existing in the crude pearlash used and in the animal matters), and converted into ferrocyanide. The boiling with water while still in the iron pot is an important and indispensable stage of the process. After filtering from the animal charcoal also produced, the solution yields crystals, having the formula, $K_4FeCy_6 3H_2O$. They are large yellow crystals, permanent in the air, if not exposed to too direct light, soluble in four parts of cold and two parts of boiling water, and insoluble in alcohol. Heated in a closed vessel, they yield potassium cyanide and ferrous carbide; and in an open vessel potassium cyanate is also formed.

A new process for making potassium ferrocyanide consists in shaking up carbon disulphide with ammonium sulphide, which forms ammonium thiocarbonate.

$$CS_2 + (NH_4)_2S = (NH_4)_2CS_3.$$

This product, heated with potassium sulphide, yields potassium thiocyanate :—

$$2(NH_4)_2CS_3 + K_2S = 2KCNS + 2NH_4HS + 3H_2S.$$

Lastly, by drying the thiocyanate, and heating it with iron, we obtain—

$$6KCNS + 3Fe_2 = K_4FeC_6N_6 + 5FeS + K_2S.$$

This process is not yet carried out on any very large scale.

Exposed for a long time to the air and strong light, potassium ferrocyanide decomposes on the surface, giving off prussic acid and becoming coated with Prussian blue. By mixing potassium ferrocyanide with soluble salts of other metals their ferrocyanides are produced by double decomposition. These reactions are very valuable in analysis, because nearly all the ferrocyanides of heavy metals form insoluble and highly characteristic precipitates. The following is a list of some of the chief precipitates thus formed :—

Reactions of Potassium Ferrocyanide.

NAME OF METAL.	COLOUR OF PRECIPITATE WITH POTASSIUM FERROCYANIDE.
Copper	Reddish-brown (chocolate).
Iron (ferrous)	White, instantly changing to pale blue.
Iron (ferric)	Dark blue.
Lead	White.
Magnesium	No effect in a fairly dilute condition.
Mercury	White.
Silver	White, gelatinous, soluble in ammonium hydrate.
Zinc	Ditto ditto.

These effects are only produced in slightly acid or perfectly neutral solutions. The two precipitates with iron deserve a special notice.

POTASSIUM FERROUS FERROCYANIDE. Formula, $K_2FeFeCy_6 = K_2Fe_2Cy_6$.

Produced when a solution of potassium ferrocyanide is mixed with a ferrous salt :—

$$K_4FeCy_6 + FeSO_4 = K_2Fe_2Cy_6 + K_2SO_4.$$

It is also a bye-product in the manufacture of hydrocyanic acid. In itself it is white, but it instantly turns blue in contact with the air. It is insoluble in hydrochloric acid but destroyed by alkalies.

FERRIC FERROCYANIDE (SYN. *Prussian Blue*). **Formula, $(Fe_2)_2 3FeCy_6$.**

Produced by adding a solution of potassium ferrocyanide to that of a ferric salt :—

$$3K_4FeCy_6 + 2Fe_2Cl_6 = (Fe_2)_2 3FeCy_6 + 12KCl.$$

It is not soluble in hydrochloric acid; but alkalies turn it brown, ferric hydrate being deposited, and ferrocyanide of the alkalies re-formed :—

$$(Fe_2)_2 3FeCy_6 + 12KHO = 3(K_4FeCy_6) + 2Fe_2 6HO.$$

It is upon the formation of Prussian blue that *Scheele's test* for hydrocyanic acid, by first adding potassium hydrate then a mixture of a ferrous and a ferric salt, and finally acidulating with hydrochloric acid, is based.

The explanation of the test is as follows (according to Gerhardt's view) :—

1. The hydrocyanic acid and the potassium hydrate form potassium cyanide.
2. The addition of the ferrous salt produces ferrous cyanide.
3. This reacting with the excess of alkali forms potassium ferrocyanide.
4. On the addition of the ferric salt, it is at first precipitated by the excess of alkali, as ferric hydrate, which on acidulation dissolves to ferric chloride, forming ferric ferrocyanide (Prussian blue) :—

$$1.\ 6HCy + 6KHO = 6KCy + 6H_2O.$$
$$2.\ 6KCy + 3FeCl_2 = 3FeCy_2 + 6KCl.$$
$$3.\ 3FeCy_2 + 4KHO = K_4FeCy_6 + 2Fe2HO.$$
$$4.\ 3K_4FeCy_6 + 2Fe_2Cl_6 = (Fe_2)_2 3FeCy_6 + 12KCl.$$

Or the whole may be shown in one equation, thus, which is quite sufficient :—

$$18KCy + 3FeCl_2 + 2Fe_2Cl_6 = (Fe_2)_2 3FeCy_6 + 18KCl.$$

(*For detection of Ferrocyanides, see Author's* **Analytical Chemistry**, *page* 66.)

METALLIC FERRICYANIDES.

FERRICYANOGEN. Formula, Fe_2Cy_{12}.

This is a radical similar to the last studied, but differing from it inasmuch as the cyanogen is combined with ferric instead of ferrous iron, and the whole radical acts as a hexad in forming salts with metals.

HYDROGEN FERRICYANIDE (SYN. *Hydroferricyanic Acid*). **Formula, $H_6Fe_2Cy_{12}$.**

Cannot be prepared like hydrogen ferrocyanide, but may be by the action of sulphuretted hydrogen on plumbic ferricyanide.

POTASSIUM FERRICYANIDE (SYN. *Red Prussiate of Potash*). **Formula, $K_6Fe_2Cy_{12}$.**

Prepared by passing chlorine gas through a dilute and cold solution of potassium ferrocyanide, forming at the same time potassium chloride :—

$$2K_4FeCy_6 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl.$$

Although not shown in the equation, there is no doubt that the chlorine also assists to convert the iron in the radical from the ferrous to the ferric state, as during the process a ferric compound is precipitated ; and the finish is indicated when this ceases to form. Potassium ferricyanide crystallized from this solution is in ruby red prismatic crystals, soluble in 4 parts of water, forming a dark greenish-yellow solution. Excess of chlorine decomposes them, as also do reducing agents such as H_2S, etc. Solutions of ferricyanide for use in analysis should be freshly made, as by exposure to the light it decomposes, being reconverted into ferrocyanide with a deposit of Prussian blue. Potassium ferricyanide is much employed in analysis, owing to its forming insoluble ferricyanides on adding it to solutions of many heavy metals. The following is a list of the most characteristic :—

Reactions of Potassium Ferricyanide.

NAME OF METAL.	COLOUR OF PRECIPITATE WITH POTASSIUM FERRICYANIDE.
Iron (Ferrous)	Dark blue (Turnbull's).
Iron (Ferric)	No precipitate.
Lead	Ditto.
Mercurous	Brownish red.
Mercuric	No effect.
Stannous	White, soluble in HCl.
Stannic	No effect.
Silver	Orange.

By the above table it is evident that potassium ferricyanide is very useful in distinguishing between various states of the same metal ;—iron, for example, with which it gives a dark blue precipitate when the salt used is ferrous, and no effect when it is ferric.

FERROUS FERRICYANIDE (SYN. *Turnbull's Blue*). **Formula, $Fe_3Fe_2Cy_{12}$.**

Produced between potassium ferricyanide and a ferrous salt :—

$$K_6Fe_2Cy_{12} + 3FeSO_4 = Fe_3Fe_2Cy_{12} + 3K_2SO_4.$$

This precipitate is insoluble in hydrochloric acid, but when treated with

potassium hydrate, or any similar alkali, it is decolorized, and deposits ferroso-ferric hydrate, forming a ferrocyanide of the alkali used in solution :—

$$Fe_3Fe_2Cy_{12} + 8KHO. = 2K_4FeCy_6 + Fe_3 8HO.$$

(*For detection of Ferricyanides, see Author's* **Analytical Chemistry**, *page* 66.)

METALLIC NITROPRUSSIDES.

These are a class of bodies obtained by the action of nitric acid on ferrocyanides and ferricyanides having the general formula $M_2(NO)FeCy_5$. They may be viewed as derived from a half molecule of a ferricyanide, M_3FeCy_6, by the displacement of one molecule of the metallic cyanide, MCy, by nitric oxide (*nitrosyl*); the latter being formed by the reducing action exercised by the ferrocyanide on the nitric acid.

SODIUM NITROPRUSSIDE. Formula, $NA_2(NO)FeCy_5.2H_2O$.

Prepared by heating five parts nitric acid and two parts potassium ferrocyanide with a little water, until a portion taken from the basin gives a slate-coloured, instead of a blue, precipitate with ferrous sulphate. The liquid having been allowed to cool (to deposit KNO_3) is filtered and neutralized with sodium carbonate, and lastly, the whole having been again filtered, is crystallized. The ruby-red crystals of sodium nitroprusside are then carefully picked out, redissolved in water, and crystallized. The solution of this salt in water is employed to detect the presence of traces of alkaline sulphides, in the presence of which it becomes of a fine violet colour.

METALLIC CYANATES.

Cyanogen can also unite with oxygen to form a class of compounds called **cyanates**. They may be viewed as nitrogen with two of its atomicities saturated by $(CO)''$ and the third by a basylous radical, thus :—

Potassium Cyanate $K'—N''' > (CO)''$

or as cyanogen in combination with an oxygenated radical of the hydroxyl type, thus :—

Potassium Cyanate $(CN)'$ $(OK)'$.

In point of fact, these two modifications actually exist, and have been named respectively *isocyanates* and *normal cyanates*.

The cyanates are of no use in pharmacy; but the following are interesting owing to their relation to urea. (See **Amides**.)

HYDROGEN CYANATE (SYN. *Cyanic Acid*). **Formula, HCNO.**

Is an exceedingly irritating colourless liquid, with a smell something between sulphurous anhydride and glacial acetic acid. It cannot be kept, as it suddenly changes of its own accord into a solid white body called *cyamelide*, which is, however, identical in composition. Cyanic acid cannot be obtained by liberation from its salts by the action of a mineral acid, as it is immediately decomposed on touching water into ammonium hydrogen-carbonate :—

$$HCNO + 2H_2O = NH_4HCO_3.$$

Cyanuric acid, $H_3C_3N_3O_3$, is a polymer of cyanic acid, from which the latter may be produced by heating to a very high temperature, thus :—

$$H_3C_3N_3O_3 = 3HCNO.$$

Cyanuric acid is prepared by heating urea till it melts. Ammonia is given off, and the acid is left as an amorphous mass, which when purified forms efflorescent crystals feebly soluble in water, containing $2H_2O$ of crystallization. It is soluble without change in the strongest sulphuric or nitric acids.

AMMONIUM CYANATE. Formula, $(NH_4)CNO$.

Is produced by synthesis from its elements by—

1. Making potassium cyanide by passing nitrogen over a mixture of carbon and potassium carbonate heated to redness.
2. Converting the potassium cyanide into potassium cyanate by fusing with an oxidizing agent such as red lead or manganic peroxide, and extracting the cyanate by boiling alcohol.
3. Mixing the alcoholic solution of potassium cyanate with ammonium sulphate, when double decomposition ensues, and the potassium sulphate, being insoluble in alcohol, is filtered out and the solution evaporated *in vacuo*.

Ammonium cyanate, if heated, immediately undergoes a molecular change, and is converted into **urea**. (*See* **Amides**.) Thus we see one of those remarkable synthetical methods by which so-called organic matter is obtained from purely inorganic constituents.

(*For detection of Cyanic and Cyanuric Acids, see Author's* **Analytical Chemistry**, *page* 65.)

METALLIC THIOCYANATES.

By the substitution of sulphur for oxygen in a cyanate, a class of salts called thiocyanates (formerly sulphocyanates) are produced, thus:—

Cyanic Acid	. HCNO,	forms	Thiocyanic Acid .	. HCNS.
Potassium Cyanate,	KCNO,	„	Potassium Thiocyanate .	KCNS.

HYDROGEN THIOCYANATE (SYN. *Sulphocyanic Acid*). **Formula, HCNS.**

Is prepared by treating plumbic sulphocyanate suspended in water with sulphuretted hydrogen. By boiling or exposure to the air, it suffers a very complex decomposition.

AMMONIUM THIOCYANATE (SYN. *Ammonium Sulphocyanate*). **Formula, NH_4CNS.**

May be obtained by the action of excess of ammonium hydrate on carbon disulphide, or by boiling ammonium cyanide with sulphur. It is also produced in the *sulphur test* for hydrocyanic acid as follows. A drop of *yellow* ammonium sulphydrate is exposed to the vapour of, or added to a solution of, hydrocyanic acid, and the whole evaporated to dryness at a very gentle heat, with the addition of a drop of ammonium hydrate. A residue is thus obtained which strikes a blood-red colour with ferric chloride, not dischargeable by hydrochloric acid, but at once bleached by solution of mercuric chloride. This colour is due to the formation of ammonium thiocyanate (which takes place when an alkaline sulphide, containing excess of sulphur, is brought into contact with cyanogen) thus:—

$$2HCy + (NH_4)_2S + S_2 = 2NH_4CyS + H_2S,$$

and subsequent production of red ferric thiocyanate.

POTASSIUM THIOCYANATE (SYN. *Sulphocyanate of Potassium*).
Formula, KCNS.

Is prepared by fusing dried **potassium** ferrocyanide with half its weight of sulphur in an iron pot, forming a mixture of potassium and ferrous thiocyanates :—

$$K_4FeC_6N_6 + 3S_2 = 4KCNS + Fe2CNS.$$

These salts having been dissolved out by water, the ferrous thiocyanate is decomposed by the careful addition of **potassium carbonate** :—

$$Fe2CNS + K_2CO_3 = 2KCNS + FeCO_3,$$

and the whole is then crystallized.

A more expensive but better process is, to add the potassium carbonate to the fused mass, and then extract with and crystallize from alcohol.

The crystals thus obtained are prismatic and anhydrous, but very deliquescent, and bitter to the taste. They are soluble in water and alcohol, and melt at a very gentle heat to a colourless liquid. When potassium thiocyanate is treated with chlorine a curious yellow insoluble body is formed, which, although at one time believed to be the radical thiocyanogen in the free state, is now called persulphocyanogen, and has a formula of H3CNS or ($C_3N_3HS_3$). The only use of potassium thiocyanate is as a reagent for the detection of ferric salts. The argentic and plumbic thiocyanates are insoluble in water.

FERRIC THIOCYANATE. Formula, $Fe_2$6CNS.

Is the cause of the red colour which is produced when any ferric salt is brought into contact with a soluble thiocyanate. It must be carefully distinguished from the similar colours by acetates, meconates, and carbolates, being known by its not being discharged by dilute hydrochloric acid, but being at once bleached by solution of mercuric chloride.

(*For detection of Thiocyanates, see Author's* **Analytical Chemistry**, *page* 65.)

COMPOUNDS OF CYANOGEN WITH THE HALOGENS.

Cyanogen unites with chlorine to produce two polymeric compounds analogous to cyanic and cyanuric acids. They are CNCl and $C_3N_3Cl_3$; the first is a gas at ordinary temperatures very pungent and soluble in water which is prepared by passing chlorine over mercuric cyanide in the dark. The second is a solid crystallizing in needles produced by exposing to sunlight a mixture of chlorine and anhydrous hydrocyanic acid. In contact with water it forms cyanuric and hydrochloric acids. Bromine and iodine form similar compounds, which are pungent volatile solids.

CHAPTER XI.

PHOSPHORUS.

PHOSPHORUS. Symbol, P. Atomic Weight, 31. Specific Gravity, 1·89. In the Free State, P_4 = 2 volumes. Molecular Weight, 124. Vapour Density, *referred to Hydrogen*, **62·9.**

This element exists chiefly in the bones of animals, in guano, and in the minerals called *apatite*, *phosphorite*, and *coprolites*, of which latter there are extensive deposits in Cambridgeshire. It is also present in nearly all the tissues of the human frame, especially the brain and nerve substance, and in animal excreta. It was discovered by Brandt, in 1669, and was prepared by slowly evaporating urine down to the consistence of honey, distilling, and purifying, with elaborate precautions. Dr. Kraft and Kunckel both made it; but it was first presented in the solid form by Ambrose Godfrey Hanckwitz, chemical assistant of the Hon. Robert Boyle. Eventually it was isolated from bones, which consist of two distinct portions, animal and mineral. The first is called *ossein*, or *cartilage*, and is isolated by steeping the bones for some time in hydrochloric acid, which dissolves out the mineral part, and leaves the *ossein* as a stiff gelatinous mass, which retains the form of the original bone. The mineral portion is called *bone earth*, and is obtained by calcining the bones in contact with the air, until all the animal portion has burned off, leaving a nearly white ash. The relative proportions in well-selected ox bones are 30 per cent. of cartilage, and 70 per cent. of bone earth. To obtain phosphorus, 3 parts of the bone earth (consisting chiefly of tricalcium phosphate, $Ca_3 2PO_4$, and calcium carbonate) are digested with 2 parts of sulphuric acid diluted with about 17 parts of water. This yields a solution of monocalcium hydrogen phosphate and a deposit of calcium sulphate, thus:—

$$Ca_3 2PO_4 + 2H_2SO_4 = CaH_4 2PO_4 + 2CaSO_4.$$

The clear solution, having been run off and concentrated to a syrup, is mixed with powdered charcoal and sand. This is transferred to an iron vessel, in which it is heated to a dull red heat. During the heating, the hydrogen and a portion of the oxygen of the monocalcium hydrogen phosphate pass off in the form of water, and a very intimate mixture of calcium metaphosphate with sand and charcoal is left:—

$$CaH_4 2PO_4 = Ca 2PO_3 + 2H_2O.$$

The whole is removed to an earthenware retort connected with a copper tube which dips into water, and distilled at a high red heat. The charcoal combines with the oxygen to form carbonous oxide and so passes off; while the silicic anhydride of the sand unites with the calcium to form calcium silicate, which remains in the retort; and the phosphorus distils over through

the copper tube into the water, at the bottom of which it collects in yellow drops:—

$$2Ca_2PO_3 + 2SiO_2 + 5C_2 = 2CaSiO_3 + 2P_2 + 10CO.$$

The crude phosphorus thus obtained is transferred to a basin containing water, and having been heated until it melts, a little potassium dichromate and sulphuric acid are stirred in. An oxidation of the impurities then takes place, and the floating matters having been skimmed off, the melted phosphorus is cast into sticks by passing it through glass tubes under water.

Phosphorus is described in the B.P. as being a semi-transparent, colourless, waxlike solid, which emits white vapours when exposed to the air. Specific gravity 1·89. It is soft and flexible at common temperatures, melts at 110°, ignites in the air at a temperature a little above its melting-point, burning with a luminous flame and producing dense white fumes. Insoluble in water, but soluble in ether and in boiling oil of turpentine.

Phosphorus ought always to be kept under water, because it takes fire when exposed to the air. The flame cannot be extinguished by water; and in case of accident the only course to pursue is to cover the burning mass with wet sand.

Besides the menstrua already mentioned, phosphorus is soluble in benzene, carbon disulphide, and fixed and essential oils. When taken from the water, wiped gently, and placed upon a dry surface, it emits a bluish-white light, and gives off fumes, which are chiefly phosphorous anhydride mixed with a little phosphoric anhydride. If a light be applied it will burn and form copious, dense, white fumes, consisting entirely of phosphoric anhydride. The phosphorus fumes emitted in contact with the air are extremely dangerous, and cause *necrosis* of the bones, chiefly attacking the jaw and smaller ankle-bones; many lucifer-match makers die miserably from this cause. When mixed with potassium chlorate or nitrate, or any peroxide, such as MnO_2 or PbO_2, phosphorus takes fire on being rubbed. It is on this principle that the action of the ordinary lucifer match is based.

Phosphorus is an allotropic body, and besides the common form can exist as:—

Red, or *amorphous phosphorus*. This modification is commercially important, and is prepared by heating the common article in a closed vessel, from which the air is entirely excluded, to a temperature of not less than 465° F., and not exceeding 485° F., for about 36 hours. In practice the phosphorus is simply placed in an iron vessel, completely closed, and furnished with a tube dipping under mercury (to act as a safety-valve, allowing the outward passage of expanded gases, but not the inward passage of air). When first heated, the contents of the vessel take fire; but the oxygen of the air being quickly exhausted, the combustion ceases, and the conversion of the remaining phosphorus goes on quickly. Red phosphorus is not soluble in carbon disulphide, nor in any of the other solvents which attack the ordinary variety; neither does it emit fumes, nor take fire spontaneously in the air. Indeed it will not inflame until heated to 500° F. It becomes luminous at 392° F., and when exposed to the air it is slowly converted into a liquid which is found to be a mixture of phosphorus and phosphoric acids, and smells of ozone.

It is of this red phosphorus that the well-known *ruby* and *safety matches* are made. In the latter it is mixed with glue and manganic dioxide, and spread upon the box, while the match is dipped only in potassium chlorate, glue, and antimonious sulphide. It is thus impossible to inflame the match on anything but the box itself.

Two new preparations of phosphorus have been introduced into the B.P.:—

1. *Oleum Phosphoratum*, prepared by heating 4 ounces of almond oil to

300°, then filtering and dissolving 12 grains of phosphorus in it at a temperature of 180° Fah.

The product is a clear but slightly coloured oil; phosphorescent in the dark.

The object of heating is to remove any water from the oil and at the same time precipitate albuminous matters. It has been stated that this oil is apt to become thick and viscid when thus prepared.

2. *Pilula Phosphori*, made by rubbing phosphorus with balsam of tolu under water at a temperature of 140° Fah., and then adding yellow wax.

The great point in the successful manufacture of this mass, is to mix when the wax is just soft and not actually fluid. It has been objected to as being very insoluble in the stomach, and the addition of a little sugar has been advised when intended for immediate consumption.

COMPOUNDS OF PHOSPHORUS WITH HYDROGEN

Phosphorus forms at least the three following compounds with hydrogen, with the first of which only the pharmacist is likely to meet:—

Gaseous	Hydrogen	Phosphide	PH_3.
Liquid	,,	,,	P_2H_4.
Solid	,,	,,	P_4H_2.

HYDROGEN PHOSPHIDE (Syns. *Phosphuretted Hydrogen. Phosphine*) **Formula, PH_3. Molecular Weight, 34. Density,** *referred to Hydrogen,* 17·5 (*theory* 17).

Is evolved when phosphorus is boiled with an alkaline hydrate in solution:—

$$3KHO + 2P_2 + 3H_2O = 3KPH_2O_2 + PH_3.$$

As thus prepared, it is usually contaminated with free hydrogen, produced by the action of excess of alkali on the potassium hypophosphite formed in the above reaction:

$$KPH_2O_2 + 2KHO = K_3PO_4 + 2H_2.$$

This may be avoided by the use of calcium, instead of potassium (or sodium) hydrate. In practice little balls of slaked lime, each containing in its centre a small fragment of phosphorus, are heated in water. As thus prepared, phosphuretted hydrogen is spontaneously inflammable in the air, and each bubble of the gas as it rises to the surface takes fire and forms beautiful rings of phosphoric acid in the form of a white smoke, which become larger and larger as they rise towards the ceiling, until they are finally dissipated.

$$PH_3 + 2O_2 = H_3PO_4.$$

It has been ascertained that the spontaneous inflammability of phosphuretted hydrogen is due to the presence of traces of the vapour of P_2H_4, and that the pure gas is not of itself inflammable in the air. The pure non inflammable gas may be prepared by the action of phosphorus on alcoholic solution of potassium hydrate.

Phosphuretted hydrogen is a natural product of the putrefaction of organic substances containing phosphorus, and is supposed to contribute to the cause of the appearance, so common in marshy districts, known as *Will o' the Wisp*. It is also evolved when a phosphite, or hypophosphite, is heated to redness.

On account of the fact mentioned in Chapter I., that the atom of phosphorus only occupies half the volume required by the theory therein explained, it follows that one molecule of phosphuretted hydrogen (two volumes) con-

tains three volumes of hydrogen and half a volume phosphorus. As, howev we cannot talk of half an atom, we are obliged to say that two molecules (fo volumes) of PH_3 contain one atom (one volume) of phosphorus, and s atoms (six volumes) of hydrogen. Phosphuretted hydrogen is colourle possesses a disgusting odour, and is very slightly soluble in water. It is al poisonous, and is very eagerly absorbed by arterial blood, from which abstracts oxygen. The odour produced in water under which phosphor has been kept, with access of light, is due in some measure to the slo production of this gas.

COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

Phosphorus combines immediately with bromine, iodine, and chlorine, to form bromide, iodide, and chloride of phosphorus. It can do so in two proportions, as follows (the preparation of the chlorides being taken as typical of that of the bromides) :—

PHOSPHOROUS CHLORIDE. Formula, PCl_3.

Prepared by slowly passing phosphorus vapour over mercurous chloride. In this compound two of the atoms of phosphorus are self-saturated, and it acts as a triad. It is an offensive liquid having a specific gravity of 1·45 and fuming in the air.

In contact with water it sinks to the bottom and is slowly decomposed, forming phosphorous and hydrochloric acids :—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

PHOSPHORIC CHLORIDE. Formula, PCl_5.

In this compound (which is a white crystalline solid) the phosphorus exercises its full (pentad) atomicity. It is prepared by passing a rapid stream of chlorine over red phosphorus. Treated with excess of water, it yields phosphoric and hydrochloric acids :—

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

When the quantity of water is limited, or it is simply exposed to moist air, it produces phosphoric oxychloride :—

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

PHOSPHOROUS OXYCHLORIDE. Formula, $POCl_3$.

Is a colourless liquid, having a specific gravity of 1·7, and boiling at 230° Fah. It has a pungent odour, and is readily decomposed by excess of water into hydrochloric and phosphoric acid. In practice it is prepared by distilling phosphoric chloride with oxalic acid or phosphoric anhydride.

The compounds of bromine with phosphorus resemble the above in preparation and properties.

Iodine forms two compounds, PI_2 and PI_3, both solid and produced by simply dissolving phosphorus and iodine in a suitable menstruum, such as carbon disulphide, and cooling till crystals form. In contact with water, phosphorous and hydriodic acids are produced. The great use of phosphorous iodide is in the making of haloid ethers. (*See* Chap. XVII.)

COMPOUNDS OF PHOSPHORUS WITH OXYGEN.

With oxygen, phosphorus forms two oxides, viz.,—

1. Phosphorous anhydride, in which it exhibits triad atomicity.
2. Phosphoric anhydride, when it acts as a pentad.

These anhydrides give rise, with water, to acids, and there is also an acid (hypophosphorous) known, without a corresponding anhydride, thus :—

Oxides.

Phosphorous Anhydride	P_2O_3
Phosphoric Anhydride	P_2O_5.

Acids.

Hypophosphorous Acid	$H_3PO_2 = (HPH_2O_2)$.
Phosphorous Acid	$H_3PO_3 = (H_2PHO_3)$.
Phosphoric Acid	H_3PO_4.

HYDROGEN HYPOPHOSPHITE (SYN. *Hypophosphorous Acid*). **Formula, HPH_2O_2.**

May be prepared by decomposing solution of baric hypophosphite with the exactly equivalent weight of sulphuric acid :—

$$Ba2PH_2O_2 + H_2SO_4 = 2HPH_2O_2 + BaSO_4.$$

It is a colourless liquid, which, on exposure to the air, is resolved into a mixture of phosphorous and phosphoric acids :—

$$4HPH_2O_2 + 3O_2 = 2H_3PO_4 + 2H_3PO_3.$$

It forms a class of salts called **hypophosphites**, which are coming into use in pharmacy, having been originally introduced as constituents in *Parrish's Chemical Food.* They are, with the exception of the silver salt, all soluble in water, and most of them dissolve in alcohol.

(*For detection of Hypophosphites, see Author's* **Analytical Chemistry**, *page* 67.)

SODIUM HYPOPHOSPHITE. Formula, $NaPH_2O_2$. Molecular Weight, 88.

Prepared by treating calcium hypophosphite with sodium carbonate, filtering the solution, evaporating and granulating at the heat of a steam bath (230° Fah.) :—

$$Ca2PH_2O_2 + Na_2CO_3 = 2NaPH_2O_2 + CaCO_3.$$

It is, when thus made, a white granular salt, having a bitter nauseous taste. It is deliquescent, very soluble in water and in spirit, but insoluble in ether. At a red heat it ignites, emitting spontaneously inflammable phosphuretted hydrogen.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 103.)

POTASSIUM HYPOPHOSPHITE. Formula, KPH_2O_2. Molecular Weight, 104.

May be prepared as the calcium salt, but using potassium hydrate, and converting the excess of the latter into carbonate, by adding potassium hydrocarbonate, and finally evaporating to dryness, then treating with alcohol, which only dissolves the potassium hypophosphite ; but the tendency of the excess of potassium hydrate to decompose the hypophosphite, as already shown (page 187) renders its preparation from calcium hypophosphite by double decomposition with potassium carbonate more desirable. It resembles sodium hypophosphite in its properties.

CALCIUM HYPOPHOSPHITE. Formula, $Ca2PH_2O_2$. Molecular Weight, 170.

Is prepared by gently heating phosphorus with water and calcium hydrate, phosphuretted hydrogen being evolved :—

$$3Ca2HO + 6H_2O + 4P_2 = 3Ca2PH_2O_2 + 2PH_3.$$

In practice it is obtained by heating phosphorus with calcium hydrate and water until phosphuretted hydrogen gas ceases to be evolved, then filtering the liquid, separating uncombined lime with carbonic acid gas, and evaporating the remaining solution until the salt separates in a crystalline condition.

It is met with as a white crystalline salt, with a pearly lustre and a bitter nauseous taste. Insoluble in rectified spirit. Soluble in six parts of cold water, and only slightly more soluble in hot water. The crystals do not lose weight when heated to 300°. Heated to redness, they ignite, evolving spontaneously inflammable phosphuretted hydrogen, and leaving a reddish-coloured residue of calcium pyrophosphate.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 104.)

BARIUM HYPOPHOSPHITE. Formula, $Ba2PH_2O_2$. Molecular Weight, 267.

Prepared like the calcium salt, taking barium hydrate instead of calcium hydrate. It is used in pharmacy for preparing quinine and magnesium hypophosphites by double decomposition with their sulphates.

PHOSPHOROUS ANHYDRIDE. Formula, P_2O_3. Molecular Weight, 110.

Referred to under **Phosphorus** as being spontaneously generated on its contact with the air. When prepared by burning phosphorus in a limited supply of air, it is a white mass, with a slight odour of garlic. Thrown into water it gives a hissing noise, and forms phosphorous acid :—

$$P_2O_3 + 3H_2O = 2H_3PO_3.$$

HYDROGEN PHOSPHITE (SYN. *Phosphorous Acid*). **Formula, H_3PO_3. Molecular Weight, 82.**

May be prepared by exploding phosphuretted hydrogen with oxygen :—

$$\begin{array}{ccccc} 2PH_3 & + & 3O_2 & = & 2H_3PO_3. \\ \text{4 vols.} & + & \text{6 vols.} & & \end{array}$$

That is to say, in the simplest ratio, two gallons of phosphuretted hydrogen require three gallons of oxygen.

It also results from the action of phosphorous chloride upon water. (*See* **PCl_3**.)

It is usually found as a syrupy fluid. It acts as a reducing agent even upon such a comparatively stable compound as sulphurous acid :—

$$3H_3PO_3 + H_2SO_3 = 3H_3PO_4 + H_2S.$$

Heated, it is converted into phosphoric acid and phosphuretted hydrogen. It forms with metals a class of salts called **phosphites**, of no great pharmaceutical interest.

(*For detection of Phosphites, see Author's* **Analytical Chemistry**, *page* 68.)

PHOSPHORIC ANHYDRIDE. Formula, P_2O_5. Molecular Weight, 142.

Produced by burning phosphorus in a glass globe, having a free supply of dry air, when it collects like a mass of snow at the bottom of the globe.

It deliquesces in the air, and eagerly unites with water, producing heat, and forming metaphosphoric acid. Theoretically it unites with water to form three varieties of phosphoric acid, although in practice the *meta* acid is the one always formed by direct union (in the cold). These three varieties are as follows:—

$P_2O_5 + H_2O = H_2P_2O_6 = 2HPO_3$ . . . *Metaphosphoric Acid.*
$P_2O_5 + 2H_2O = H_4P_2O_7$ . . . . . *Pyrophosphoric Acid.*
$P_2O_5 + 3H_2O = H_6P_2O_8 = 2H_3PO_4$ . . . *Orthophosphoric Acid.*

HYDROGEN PHOSPHATE (SYNS. *Orthophosphoric Acid. Acidum Phosphoricum, B.P.*) **Formula, H_3PO_4. Molecular Weight, 98.**

Prepared by boiling phosphorus in very dilute nitric acid. The action is one of direct oxidation, nitric oxide being evolved:—

$$3P_2 + 10HNO_3 + 4H_2O = 6H_3PO_4 + 10NO.$$

The B.P. directs the operation to be made in a retort furnished with a condenser at a gentle heat till the phosphorus is dissolved, returning the condensed nitric acid and water to the retort from time to time. The liquid is then transferred to a porcelain dish and evaporated until it is reduced to four fluid ounces; next it is removed to a platinum vessel, and the evaporation continued until orange-coloured vapours are no longer formed. The strong syrupy acid thus obtained is diluted to the proper strength, viz., =13·5 per cent. H_3PO_4 (= 10 per cent. P_2O_5).

It is noticeable that at the end of the preparation the acid is found, *not* in the receiver, but in the retort. This is because phosphoric acid *is not volatile*, and the action is simply one of boiling, instead of distillation. The object of using a receiver is to condense the water and nitric acid which may boil off, so that they may be returned from time to time to the retort, to keep up uniform and continued action without loss of material. The acid, when transferred from the retort, always contains H_3PO_3, which is only finally changed during concentration in a porcelain dish. The process ought, therefore, to be represented in two steps, thus:—

$$2HNO_3 + P_2 + 2H_2O = 2H_3PO_3 + 2NO.$$
$$3H_3PO_3 + 2HNO_3 = 3H_3PO_4 + 2NO + H_2O.$$

Acidum phosphoricum, B.P., is a colourless liquid, with a sour taste and strongly acid reaction. Specific gravity, 1·08. With ammonio-nitrate of silver it gives a canary yellow precipitate, soluble in ammonium hydrate and in diluted nitric acid. Evaporated, it leaves a residue, which melts at a low red heat, and upon cooling exhibits a glassy appearance (metaphosphoric acid).

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 104.)

When phosphoric acid is evaporated to dryness, it first loses one molecule of water, and at 430° F. becomes pyrophosphoric acid:—

$$2H_3PO_4 - H_2O = H_4P_2O_7.$$

This residue, if further heated to redness, again loses water, and is converted into metaphosphoric acid:—

$$H_4P_2O_7 - H_2O = 2HPO_3.$$

The intermediate step is difficult to obtain. In forming the class of salts called *orthophosphates*, PO_4 acts as a triad radical.

HYDROGEN PYROPHOSPHATE (SYN. *Pyrophosphoric Acid*). **Formula, $H_4P_2O_7$.**

Is a soft substance of a glassy nature, which may be prepared, although not quite pure, by evaporating phosphoric acid, and heating to 430° F. until, on dissolving a portion in a little cold water, it ceases to give a yellow precipitate with argentic nitrate. Another method is to heat disodium hydrophosphate until it is entirely converted into sodium pyrophosphate :—

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

The residue thus obtained, if digested with a salt of lead, forms plumbic pyrophosphate, which may then be suspended in water, and treated with sulphuretted hydrogen :—

$$Pb_2P_2O_7 + 2H_2S = H_4P_2O_7 + 2PbS.$$

It forms salts called *pyrophosphates*, having the radical P_2O_7 acting as a tetrad. By boiling with water it is converted into *ortho-*, and, by heating to redness, into *meta-* phosphoric acid.

(*For detection of Pyrophosphates, see Author's* **Analytical Chemistry**, *page* 68.)

HYDROGEN METAPHOSPHATE (SYNS. *Metaphosphoric Acid. Glacial Phosphoric Acid*). **Formula, HPO_3.**

A hard glassy substance which dissolves thoroughly, but not rapidly, in water. It is prepared by evaporating the B.P. acid, and heating the residue to redness. By continued boiling with water it recombines, yielding the B.P. acid. It forms a class of salts called **metaphosphates**, in which PO_3 acts as a monad.

(*For detection of Metaphosphates, see Author's* **Analytical Chemistry**, *page* 68.)

The three varieties of phosphoric acid may be thus distinguished :—

Phosphoric Acids.	With Argent-ammonium Nitrate.	With Albumen.
Orthophosphoric Acid .	Gives a yellow precipitate.	No effect.
Pyrophosphoric Acid . .	Gives a white precipitate.	No effect.
Metaphosphoric Acid .	Gives a white precipitate.	Is coagulated.

Orthophosphates are very complex in the possible variety of their formulæ, because with the triad radical both monad and dyad bases may form hydrogen salts.

For example, in theory, with sodium we might have :—

Na_3PO_4	Trisodium Phosphate.
Na_2HPO_4	Disodium Hydrogen-phosphate.
NaH_2PO_4	Monosodium Hydrogen-phosphate.

With calcium we might have :—

Ca_32PO_4	Tricalcium Phosphate (basic).
$Ca_2H_22PO_4 = 2CaHPO_4$.	Dicalcium Hydrogen-phosphate (neutral).
CaH_42PO_4	Monocalcium Hydrogen-phosphate (acid).

DIAMMONIUM HYDROGEN-PHOSPHATE (Syn. *Phosphate of Ammonia*). **Formula, $(NH_4)_2HPO_4$. Molecular Weight, 132.**

May be formed by mixing phosphoric acid with a slight excess of ammonium hydrate.

It may also be directly prepared from bone ash by a similar process to that employed for disodium hydrogen phosphate, using ammonium carbonate instead of sodium carbonate.

It is in transparent colourless prisms, soluble in water, but insoluble in spirit. When heated, it evolves ammonia gas, and leaves a residue of glacial phosphoric acid.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 104.)

DISODIUM HYDROGEN-PHOSPHATE (Syns. *Tribasic Phosphate of Soda. Sodæ Phosphas, B.P.*) **Formula, $Na_2HPO_4 12H_2O$. Molecular Weight, 358.**

Is prepared by digesting bone earth in sulphuric acid, forming monocalcium hydrogen-phosphate in solution, and depositing calcium sulphate:

$$Ca_3 2PO_4 + 2H_2SO_4 = CaH_4 2PO_4 + 2CaSO_4.$$

The pasty mass is then treated with water, and the removal of the calcium sulphate ensured by filtration and concentration. The clear solution of monocalcium hydrogen phosphate thus obtained is treated with sodium carbonate, which causes a precipitate of dicalcium hydrogen phosphate, and leaves disodium hydrogen-phosphate in solution:—

$$CaH_4 2PO_4 + Na_2CO_3 = Na_2HPO_4 + CaHPO_4 + CO_2 + H_2O.$$

The deposited phosphate is by no means absolutely constant, but often contains tricalcium phosphate.

Sodæ Phosphas, B.P., is in transparent, colourless, rhombic prisms, terminated by four converging planes, efflorescent, tasting like common salt; it is soluble in water, its solution having a faintly alkaline reaction. When this salt is heated to redness it yields sodium pyrophosphate:—

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

By boiling with water, that salt may be again changed to the original disodium hydrogen-phosphate.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 104.)

AMMONIUM and SODIUM HYDROGEN-PHOSPHATE (Syn. *Microcosmic Salt*). **Formula, $Na(NH_4)HPO_4 4H_2O$.**

Formed by dissolving seven parts of disodium hydrogen phosphate and one part of ammonium chloride in two parts of boiling water, and crystallizing. This salt is used extensively in blowpipe analysis, because on heating, it evolves ammonia and water, leaving pure sodium metaphosphate. Thus produced, it has the power of dissolving metallic oxides, many of which cause it to assume very characteristic colours. To perform such experiments, a little of the salt is placed in a loop of platinum wire, and heated with the blow-pipe till a clear bead is obtained. The bead is then touched with the powder to be analyzed, and again ignited, first in the inner, and then in the outer flame, and examined after each heating, when the following effects, among others, may be observed.

Blowpipe Reactions of Microcosmic Salt.

Colour of Bead.	In the Inner Flame.	In the Outer Flame.
Blue	Cobalt only	Cobalt and Copper.
Amethyst . .	. . . .	Manganese.
Red	Copper	Iron.
Green. . . .	Chromium	Chromium.

Silica floats about in the bead in undissolved particles, and silver produces an opalescent appearance.

AMMONIUM MAGNESIUM-PHOSPHATE. Formula, $MgNH_4PO_4$.

A white crystalline precipitate produced between magnesium sulphate and a soluble phosphate in the presence of ammonium hydrate, ammonium chloride having been previously added to prevent the precipitation of magnesium hydrate :—

$$MgSO_4 + NH_4HO + Na_2HPO_4 = MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

It is slightly soluble in cold water, and forms very slowly in dilute solutions. Its production is much accelerated by stirring with a glass rod; and after collection it must be washed with water containing ammonium hydrate, in which it is almost insoluble.

By strong ignition it is converted into magnesium pyrophosphate ($Mg_2P_2O_7$).

It is in this form that phosphoric acid is usually precipitated and weighed. 222 parts of $Mg_2P_2O_7$ = 142 parts P_2O_5, or 234 parts "*soluble phosphate of lime*," or 310 parts "*bone earth rendered soluble.*"

(*See Gravimetric Quantitative Analysis, in Author's* **Analytical Chemistry**, *page* 179.)

TRICALCIUM PHOSPHATE (Syns. *Tribasic Phosphate of Calcium. Calcis Phosphas, B.P.*) **Formula, Ca_32PO_4. Molecular Weight, 310.**

Is prepared by dissolving bone ash in hydrochloric acid, monocalcium hydrogen-phosphate and calcium chloride being formed :—

$$Ca_32PO_4 + 4HCl = CaH_42PO_4 + 2CaCl_2;$$

and then filtering from insoluble matters and reprecipitating with ammonium hydrate.

$$CaH_42PO_4 + 2CaCl_2 + 4NH_4HO = Ca_32PO_4 + 4NH_4Cl + 4H_2O.$$

The precipitate is then washed and dried at 212° Fah.

Calcis phosphas, B.P., is a light, white, amorphous powder, insoluble in water, but soluble without effervescence in diluted nitric acid. The solution continues clear when an excess of acetate of soda is added to it, because this phosphate is soluble in all ordinary acids, and even in acetic acid, in which the phosphates of aluminium and iron are insoluble. It is unaltered by heat, and is the form in which phosphorus is found in bone ash.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 105.)

DICALCIUM HYDROGEN PHOSPHATE. Formula, $Ca_2H_22PO_4$, *or* $CaHPO_4$.

This is the truly neutral, or simplest, combination of calcium and phosphoric acid. It is deposited as a gelatinous precipitate when disodium hydrogen-phosphate is added to an acid solution of calcium chloride, and also in the last stage of the B.P. manufacture of *sodæ phosphas*.

MONOCALCIUM HYDROGEN PHOSPHATE (Syn. *Superphosphate of Lime*). **Formula, CaH_42PO_4. Molecular Weight, 234.**

Is produced whenever tricalcium phosphate is acted upon by an acid capable of effecting its solution. This phosphate is the chief active principle of artificial manures, and it is on the amount of this constituent that their main value depends for fertilizing purposes. It is known in trade as *soluble phosphate*, or *superphosphate of lime*.

The estimation of the amount of soluble phosphate in a manure is an important operation.

(*See Gravimetric Quantitative Analysis, in Author's* **Analytical Chemistry**, *page* 179.)

TRIFERROUS PHOSPHATE (Syns. *Ferri Phosphas. Tribasic Phosphate of Iron*). **Formula, Fe_32PO_4.**

Prepared by precipitating **ferrous sulphate** with **disodium hydrogen-phosphate** in the presence of **sodium acetate**, washing the precipitate, and drying it at 120° F. :—

$$3FeSO_4 + 2Na_2HPO_4 + 2NaC_2H_3O_2 = Fe_32PO_4 + 3Na_2SO_4 + 2HC_2H_3O_2.$$

The sodium acetate is added to ensure the formation of triferrous phosphate, by combining with the excess of SO_4 and liberating instead acetic acid, in which it is insoluble. If it were not employed, **ferrous hydrogen phosphate** would be formed, thus :—

$$3FeSO_4 + 3Na_2HPO_4 = 3FeHPO_4 + 3Na_2SO_4.$$

On adding the acetate, this hydrogen phosphate is all converted into triferrous phosphate.

$$3FeHPO_4 + 2NaC_2H_3O_2 = Fe_32PO_4 + Na_2HPO_4 + 2HC_2H_3O_2.$$

Ferri phosphas, B.P., is met with as a slate-blue amorphous powder, insoluble in water and acetic acid, but soluble in hydrochloric acid. It is reprecipitable from its solution by the addition of excess of an alkaline hydrate or acetate. The addition, however, of a little citric or tartaric acid prevents its reprecipitation by ammonium hydrate. By heat it is changed into ferric phosphate in contact with the air.

When first precipitated, triferrous phosphate is white, but turns to a slate-blue on contact with the air, and as usually sold it is therefore really a complex compound, having the formula $(Fe_32PO_4)_3(FePO_4)_2Fe_2O_3 16H_2O$. It has also been stated, that if the iron salt be added to the disodium hydrogen-phosphate, instead of *vice versâ*, the production of ferrous hydrogen phosphate cannot be prevented.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 105.)

FERRIC PHOSPHATE (SYN. *Perphosphate of Iron*). **Formula, $FePO_4$ Molecular Weight, 151.**

Is produced as a white precipitate on mixing the solution of a soluble phosphate with ferric chloride in the presence of ammonium acetate. This reaction enables us to separate small quantities of phosphoric acid from all other metals.

BISMUTHOUS PHOSPHATE. Formula, $BiPO_4$. Molecular Weight, 303.

Is a white precipitate formed when solution of bismuthous nitrate is added to a soluble phosphate. It is insoluble in nitric acid, and is used frequently for the separation of phosphoric acid from other metals. It fails in accuracy, however, in the presence of much aluminium and iron.

AMMONIUM PHOSPHO-MOLYBDATE.

Is formed as a yellow precipitate when solution of ammonium molybdate in nitric acid is added to a soluble phosphate. This is the most accurate process for the separation of phosphoric acid from all metals. It is performed in practice as follows :—the sample is dissolved in nitric acid, a large excess of ammonium molybdate dissolved in nitric acid is added, and the whole is allowed to stand for twelve hours in a warm place. The precipitated ammonium phospho-molybdate is collected, washed with water containing a little of the precipitant, and then dissolved in ammonium hydrate. The solution thus obtained is then ready for treatment with the ordinary process.

(*See Gravimetric Quantitative Analysis in Author's* **Analytical Chemistry**, *page* 179.)

This process is not effectual in the presence of arsenic or silicic acid. The following is the composition of ammonium phospho-molybdate dried at 212°F., as given by Muntzinger.

Phosphoric Acid	3·962
Ammonium Oxide	3·577
Molybdic Acid	92·461
	100·000

COMPOUNDS OF PHOSPHORUS WITH SULPHUR.

By heating amorphous phosphorus with sulphur, a very rapid and violent reaction takes place; and, according to the quantities of each element used, the following series of compounds can be made :—

Hemisulphide	P_4S.
Monosulphide	P_2S.
Sesquisulphide	P_4S_3.
Trisulphide	P_2S_3.
Pentasulphide	P_2S_5.
Dodecasulphide	P_2S_{12}.

None are of interest in medicine or pharmacy.

CHAPTER XII.

ARSENIC.

ARSENIC (SYN. *Arsenicum*). **Symbol, As. Atomic Weight, 75. In the Free State, As_4 = 2 volumes. Molecular weight, 300. Vapour Density,** *referred to Hydrogen*, **153** *at* **860° C**; *referred to Air*, **10·6.**

This metalloid is one of the most extensively distributed substances in nature, although usually in small quantities. It is found native in silver and tin ores, also in the form of the yellow sulphide called *orpiment* (As_2S_3) and the red sulphide called *realgar* (As_2S_2).

Its most abundant source, is the mineral commonly called *arsenical iron pyrites* (ferric sulpharsenide, $Fe_2''S_2''As_2$, or $2FeSAs$), from which it may be obtained by sublimation, out of contact with the air. On a small scale it may be produced by heating arsenious anhydride with a mixture of dried sodium carbonate and potassium cyanide in a dry test-tube the mouth of which is lightly closed by the thumb, when arsenic will form as a *mirror* inside the tube. Arsenic is a solid, crystallizing in octahedra, and volatilizing at 356° F., without previously fusing. It has a brilliant metallic lustre, which, however, rapidly tarnishes in the air; and its vapour is of a yellowish tinge, and possesses a peculiar, garlic like, odour. When heated in the air, it rapidly absorbs oxygen and deposits a crystalline sublimate of arsenious anhydride. It combines directly with chlorine, bromine, and iodine; and so energetic is the action, that powdered arsenic introduced into chlorine gas suddenly inflames, producing thick white fumes of arsenious chloride.

Metallic arsenic is sometimes used in veterinary medicine, and is very poisonous, but not so much so as arsenious anhydride.

(*For detection of Arsenic in cases of poisoning, see Author's* **Analytical Chemistry**, *page* 144; *for the general reactions and separation, see page* 33.)

HYDROGEN ARSENIDE (SYNS. *Arseniuretted Hydrogen. Arsenamine*). **Formula, AsH_3. Molecular Weight, 78. Density,** *referred to Hydrogen*, **39. Density,** *referred to Air*, **2·695.**

Is a very poisonous, colourless gas, with a strong garlic odour, which is produced whenever an easily reducible compound of arsenic (such as arsenious anhydride) is brought into contact with nascent hydrogen, generated by a mixture of zinc and dilute sulphuric or hydrochloric acid. Taking the above mentioned substance, the reaction would be :—

$$As_2O_3 + 6H_2 = 2AsH_3 + 3H_2O.$$

Mixed with excess of oxygen, and an electric spark passed, it explodes, forming arsenious anhydride and water.

$$\underset{4\ \text{vols.}}{2AsH_3} + \underset{6\ \text{vols.}}{3O_2} = As_2O_3 + 3H_2O.$$

The fact that arsenic in the state of vapour only occupies half the space of an atom of hydrogen, shows that two volumes (one molecule) of arseniuretted hydrogen must contain three volumes of hydrogen and half a volume of arsenic.

When a light is applied to the gas as it issues from a jet, it takes fire, and burns with a long, narrow, greenish flame, producing copious fumes of arsenious anhydride.

Arseniuretted hydrogen is decomposable by heat; and when a current of it is passed through a tube heated to dull redness, a dark ring of metallic arsenic is deposited inside the tube.

When compounds containing antimony are brought into contact with zinc and dilute sulphuric acid, a very similar gas is produced, called antimoniuretted hydrogen (SbH_3). In general behaviour, this latter gas is extremely like arseniuretted hydrogen, except that it is inodorous, and its flame has a bluish tint. These two gases may be readily distinguished by passing them into solution of argenic nitrate, when the arseniuretted hydrogen will become decomposed, forming arsenious acid, which will remain in solution; while the chief product of the decomposition of the antimoniuretted hydrogen will be argentic antimonide, which will deposit. In the case of arseniuretted hydrogen, the reaction is:—

$$6AgNO_3 + 3H_2O + AsH_3 = 6HNO_3 + H_3AsO_3 + 3Ag_2.$$

With the antimoniuretted hydrogen, the following decomposition occurs:—

$$3AgNO_3 + SbH_3 = 3HNO_3 + Ag_3Sb.$$

Another very marked distinction consists in the fact, that while arseniuretted hydrogen is evolved on adding arsenical solution to a heated mixture of zinc and solution of potassium hydrate, it is not possible to produce antimoniuretted hydrogen in that way. This is sometimes attributed to the fact that the antimony compounds are thrown down in an insoluble form by the action of the alkali, and so it is prevented from combining with the nascent hydrogen; but the true explanation is doubtless to be found in the much greater stability possessed by the oxides of antimony over those of arsenic.

When arseniuretted hydrogen is passed into a solution of a cupric salt, it deposits cupric arsenide:—

$$6CuSO_4 + 4AsH_3 = 6H_2SO_4 + 2Cu_3As_2.$$

It acts generally as a reducing agent; and when passed into a mercuric solution it produces the corresponding mercurous salt, and deposits metallic arsenic:—

$$6HgCl_2 + 2AsH_3 = 3Hg_2Cl_2 + 6HCl + As_2.$$

In addition to the gaseous compound just described, a solid hydride of arsenic has been prepared, to which the formula As_4H_2 has been assigned. The remaining metallic arsenides are of no great interest to pharmacists.

ARSENIOUS ANHYDRIDE (Syns. *Anhydrous Arsenious Acid. Acidum Arseniosum. White Arsenic*). **Formula, As_2O_3. Molecular Weight, 198. Vapour Density,** *referred to Hydrogen*, **188.** *Theory*, **198. Vapour Density,** *referred to Air*, **13. Specific Gravity, 3·6** *to* **3·7.**

Is obtained during the roasting of arsenical iron pyrites, and other ores containing arsenic. The metal volatilizes, combines with the oxygen of the air, and deposits as arsenious anhydride in long tubes, or in chambers, provided for the purpose. The deposit consists of the anhydride in a very finely-divided state, called by the workmen *flour of arsenic*. This is submitted to

resublimation, and the sublimate received in cylinders, where it collects in masses, which are broken up and sold as *vitreous arsenic*.

These lumps gradually lose their glassy appearance, and become like masses of porcelain, but usually retain here and there streaks of the vitreous arsenious anhydride which has not suffered alteration. Vitreous arsenious anhydride is amorphous; but when it becomes opaque and porcelain-like, it changes to the crystalline form, and is then found to crystallize in octahedra, and when sublimed in a small tube it deposits as a white ring of opaque crystals having that form. The specific gravity of the vitreous anhydride is 3·78 and of the crystalline, 3·68. The former variety is also soluble in 25 parts of cold water, while the latter requires 80 parts of the same menstruum. Both are insoluble in ether, and only slightly soluble in alcohol; but while the former dissolves better in strong than in dilute spirit, the case is just reversed with the latter.

Arsenious anhydride is called (but erroneously) *acidum arseniosum* in the B.P., and is thus described by that authority:—

Occurs as a heavy white powder, or in sublimed masses which usually present a stratified appearance, caused by the existence of separate layers differing from each other in degrees of opacity. When slowly sublimed in a glass tube, it forms minute brilliant and transparent octahedral crystals. It is sparingly soluble in water, and its solution gives with ammonio-nitrate of silver a canary-yellow precipitate insoluble in water, but readily dissolved by ammonia and by nitric acid. Sprinkled on a red-hot coal, it emits an alliaceous odour. It is entirely volatilized at a temperature not exceeding 400° F.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 105.)

Arsenious anhydride is an exceedingly powerful poison, the antidotes to which are calcium hydrate, magnesium oxide, and ferric hydrate, the latter being by far the best. All three act by forming insoluble arsenites, the ferric arsenite being the least easily dissolved. (*For particulars of the conditions, for using ferric hydrate, see* **Ferric Arsenite**.)

An aqueous solution of arsenious anhydride, in consequence partly of its sparing solubility in cold water, displays only a slightly acid behaviour towards litmus paper, and does not possess any marked taste. If it be heated with *black flux*, or a mixture of potassium cyanide and sodium hydrocarbonate, or simply powdered charcoal, arsenic is evolved, and condenses on the cool part of the vessel as a metallic coating. When cupr-ammonium sulphate is added to the solution, green cupric arsenite falls. (*For other tests, see* **Arseniuretted Hydrogen**.)

When copper is boiled with strong hydrochloric acid, arsenious anhydride, and water, a deposit of cupric arsenide is formed upon the metal, and it is on this fact that *Reinsch's test* depends for its success. The deposit is decomposed by heating in an open tube, when it gives rise to a sublimate of minute octahedra of arsenious anhydride.

The addition of a mineral acid, especially hydrochloric, augments greatly the solubility of arsenious anhydride in water. When a solution of the vitreous variety is made in boiling dilute hydrochloric acid, and allowed to crystallize in the dark, the production of the crystals is observed to take place accompanied by a small flash of light. This effect is more visible if the crystallization be hastened by shaking the vessel. Arsenious anhydride is also very soluble in solutions of alkaline carbonates, and both these facts are taken advantage of in the following B.P. preparations:—

1. *Liquor Arsenici Hydrochloricus.* Prepared by boiling 80 grains of arsenious anhydride in four ounces of water with 2 drachms of hydrochloric acid, and making up to 1 pint with water.

Thus made, *Liquor Arsenici Hydrochloricus* is a colourless liquid, having an acid reaction. Specific gravity, 1·009.

When arsenious anhydride is boiled with water and hydrochloric acid in anything like the proportions recommended above, no combination occurs. The only mode of causing the two bodies to unite, is to distil them without diluting the acid in the least.

2. *Liquor Arsenicalis* (SYN. *Fowler's Solution*). Prepared by placing 80 grains of arsenious acid and carbonate of potash respectively in a flask with ten ounces of the water, and applying heat until a clear solution is obtained. Allow this to cool. Then add 5 fluid drachms of compound tincture of lavender, and as much distilled water as will make the bulk one pint. The result is a reddish liquid, alkaline to test-paper, and having the odour of lavender. Specific gravity, 1·009.

Made as thus directed, *liquor arsenicalis* is simply a solution of arsenious anhydride in potassium carbonate. If, however, the solution were stronger and the boiling continued longer, a compound could be formed, having the formula $2KH_2AsO_3.As_2O_3$.

Arsenious anhydride is estimated according to the B.P. by means of *volumetric solution of iodine.* This solution acts as an indirect oxidizer, converting it into arsenic acid, the following reaction occurring:—

$$As_2O_3 + 5H_2O + 2I_2 = 2H_3AsO_4 + 4HI.$$

Thus it is plain that one molecular weight of arsenious acid represents four atomic weights of iodine.

(*See Volumetric Quantitative Analysis, in Author's* **Analytical Chemistry**, *page* 157.)

Arsenious anhydride is supposed to form arsenious acid, H_3AsO_3, in contact with water; but the acid has not been isolated.

Displacement of its hydrogen by basylous radicals produces a class of salts called **arsenites**, of which there are several varieties, as in the case of phosphites and phosphates. Thus we have (M, being any monad metal):—

Arsenites	$M_3'AsO_3'''$.
Pyroarsenites	$M_4'As_2O_5^{iv}$.
Metarsenites	$M'AsO_2'$.

The different salts known as arsenites are, however, insufficiently defined to render it convenient to establish the distinction which is theoretically desirable. Ammonium arsenite in solution is entirely decomposed by evaporation, the acid being deposited in a pure condition, and ammonium hydrate being evolved. Potassium and sodium arsenites are alkaline in reaction whatever may be the amount of the arsenious anhydride they contain. Calcium, strontium, and barium oxides form soluble salts on boiling with arsenious anhydride (in excess) and water. On acting upon the solutions thus produced with the hydrates of the same metals, hydrato- (or oxy-) salts are produced, soluble like the hydrates in salts of ammonium, and also in acids. Silver, magnesium, and dyad, triad, tetrad, pentad, and hexad metals form insoluble arsenites, all of which may be procured by precipitation, except when ammonium salts, free hydrochloric acid, and in some cases free acetic acid, are present.

(*For detection of Arsenites, see Author's* **Analytical Chemistry**, *page* 71.)

CUPRIC ARSENITE (SYN. *Scheele's Green*). **Formula, $CuHAsO_3$ *or* Cu_32AsO_3.**

One or other of these two bodies is precipitated—

1. When an **alkaline arsenite** is mixed with a **cupric solution**:—

$$K_2HAsO_3 + CuSO_4 = CuHAsO_3 + K_2SO_4.$$

2. When solution of pure **arsenious acid** is treated with cuprammonium sulphate free from excess of ammonia. This reaction is best performed by adding a little cupric sulphate to the suspected solution of arsenious acid, and then dropping in very dilute ammonium hydrate with great care until the precipitate forms.

The second of the two greens is the brighter in colour, and both are soluble in the least excess of acid or alkali. A solution in excess of potassium hydrate alters rapidly, depositing *cuprous* hydrate, and leaving potassium *arseniate* in solution, the arsenious acid oxidizing itself at the expense of the cupric salt.

A modification of Scheele's green, commonly termed Schweinfurth, mitis, or imperial green, and when not so pure, Brunswick green, is prepared by boiling verdigris with arsenious acid and water. It is truly a cupric acetometarsenite, and is much employed for colouring wall papers, to the detriment of the health of persons inhabiting the rooms so ornamented. This poisonous effect is doubtless owing to minute particles detaching themselves from the paper and floating in the air. The dangers of arsenical wall papers are undoubted, although perhaps somewhat exaggerated in the minds of many.

FERRIC OXYARSENITE. Formula Indefinite.

Is most probably the compound the formation of which renders ferric hydrate the most valuable antidote to arsenical poisoning. For this purpose fourteen parts of ferric hydrate must be employed to one part of the arsenious anhydride supposed to be present. Arsenious anhydride does not combine with the ferric hydrate unless freshly prepared; and it is therefore always advisable to produce it at the instant of administration. Because of the purgative power of magnesium salts tending to work off the insoluble ferric oxyarsenite, it is best to precipitate the ferric hydrate with magnesium oxide (*magnesia, B.P.*) or magnesium oxycarbonate which has been heated until a portion only is converted into oxide. Sodium or potassium hydrates or carbonates may also be used; but ammonium hydrate must not be employed, because of the marked solubility of the ferric oxyarsenite in ammoniacal salts. A quarter of an ounce of magnesium oxide (or three times the quantity of ordinary washing soda in crystals) will take two or three times its amount of the official *liquor ferri perchloridi fortior*, and will render innocuous a dozen grains or more of the arsenious anhydride.

ARSENIC ANHYDRIDE (SYNS. *Anhydrous Arsenic Acid. Pentoxide of Arsenic*). **Formula, As_2O_5. Molecular Weight, 230.**

Is prepared,—

1. By strongly heating the arsenic acid.

2. By heating arsenious oxide with nitric acid, and decomposing the arsenic acid formed at a high temperature.

3. By evaporating to dryness, and heating the residue of a solution of arsenious oxide through which chlorine gas has been passed. The reaction in the last case would be:—

$$1.\ As_2O_3 + 5H_2O + 2Cl_2 = 2H_3AsO_4 + 4HCl.$$

$$2.\ 2H_3AsO_4 = As_2O_5 + 3H_2O.$$

A strong red heat splits up arsenic anhydride into arsenious anhydride and oxygen, the former at the same time volatilizing. Thus no residue is left.

HYDROGEN ARSENIATE (SYN. **Arsenic Acid**). **Formula, H_3AsO_4. Molecular Weight, 142.**

May be prepared

1. By dissolving arsenious anhydride in nitric acid, evaporating to dryness, and moistening with a little more nitric acid, in order to ensure complete conversion. The reaction would be:—

$$As_2O_3 + 2H_2O + 2HNO_3 = 2H_3AsO_4 + N_2O_3.$$

2. By passing chlorine into a solution of arsenious anhydride, when the decomposition represented under arsenic anhydride occurs.

3. When a solution of iodine acts upon arsenious anhydride, likewise in solution, the action being:—

$$As_2O_3 + 5H_2O + 2I_2 = 2H_3AsO_4 + 4HI.$$

4. When hydrochloric and nitric acids are unitedly made to oxidize arsenious anhydride, the hydrochloric acid converting it into arsenious chloride, and the nitric acid transforming the greater part of this into arsenic acid. The two steps will be:—

1. $As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O.$

2. $2AsCl_3 + 5H_2O + 2HNO_3 = 2H_3AsO_4 + N_2O_3 + 6HCl.$

The solutions obtained in the above modes deposit, at the ordinary atmospheric temperature, crystals containing one molecule of water of crystallization, which are very deliquescent, and consist of prismatic and transparent plates. If these be fused at 212° F. they yield the true acid, H_3AsO_4. At about 300° F. this acid gives off half an equivalent of water, and yields pyroarsenic acid, thus:—

$$2H_3AsO_4 = H_4As_2O_7 + H_2O.$$

Unlike the tri-hydrated acid, the solution of this acid (pyroarsenic) in water is attended with considerable development of heat. At 403° F. pyroarsenic acid yields a salt-like mass of $HAsO_3$ (metarsenic acid). Arsenic acid is strongly corrosive, and attacks the cuticle, producing blisters. It is employed in dyeing to set free chlorine from calcyl chloride. A mixture of arsenic acid and gum is painted in patterns upon a coloured article, and when this is immersed in what is termed "the chloride of lime vat," the chlorine set free by the acid bleaches the part of the material which has been thus treated.

Arsenic acid and arseniates are less powerful as destroyers of life than the arsenites and arsenious acid. Although arsenic acid resembles phosphoric acid in many particulars, it differs from it in the ease with which the products of the action of heat upon it (arsenic anhydride, metarsenic acid, and pyroarsenic acid) take up water, re-forming the true or ortho-acid. Pure arsenic acid in solution acts upon iron and zinc exactly like dilute sulphuric acid, liberating hydrogen, but in the presence of an acid it is advisable to employ an alkaline acetate, so that the only free acid may be acetic, in which arseniates do not as a rule dissolve. An example of this is seen in the manufacture of *ferri arsenias, B.P.*

Arseniates require the addition of hydrochloric acid to their solutions, previous to forming a precipitate with sulphuretted hydrogen; and the gas must be passed for a long time, as precipitation does not occur until the whole is first reduced to the arsenious condition.

A great analogy obtains between arseniates and phosphates, and also between arsenic and phosphoric anhydrides, both of which may be used to produce many anhydrides of "organic" acids, owing to their powerful affinity for water. The crystallizable salts of the two radicals are isomorphous.

Thus there are two salts of sodium containing, respectively, twelve and seven molecules of water of crystallization.

These are—

Disodium Orthophosphates:—

$$Na_2HPO_4.12H_2O, \text{ and } Na_2HPO_4.7H_2O.$$

With which are comparable—

Disodium Orthoarseniates:—

$$Na_2HAsO_4.12H_2O, \text{ and } Na_2HAsO_4.7H_2O.$$

Both of the $12H_2O$ salts form prismatic crystals, the arrangement of the seven molecule salt being rhombic.

All neutral arseniates give a brick-red precipitate with argentic nitrate, which serves to distinguish them from either arsenites or phosphates.

(*For detection and separation of Arseniates, see Author's* **Analytical Chemistry**, *page* 72.)

DIAMMONIUM HYDROGEN-ARSENIATE (SYN. *Arseniate of Ammonium*). **Formula, $(NH_4)_2HAsO_4$.**

Is produced by adding ammonium hydrate to arsenic acid to slight alkaline reaction:—

$$H_3AsO_4 + 2NH_4HO = (NH_4)_2HAsO_4 + 2H_2O.$$

The solution cannot be evaporated by heat without decomposition and production of monammonium hydrogen-arseniate, $NH_4H_2AsO_4$, so spontaneous deposition of crystals must be allowed to take place by simply exposing the solution to the air in a warm place. These crystals themselves decompose by exposure to the air, becoming efflorescent and evolving ammonia gas. The solution of diammonium hydrogen-arseniate may be often used with advantage in analysis, instead of the corresponding disodium hydrogen phosphate, as a precipitant for magnesium. When evaporated to dryness and heated, it entirely decomposes into a set of volatile products, viz., nitrogen, ammonia gas, arsenic, and water.

DISODIUM HYDROGEN-ARSENIATE (SYN. *Sodæ Arsenias*). **Formula, Na_2HAsO_4. Molecular Weight, 186.**

Is prepared by fusing together arsenious anhydride, sodium carbonate, and sodium nitrate, forming sodium pyroarseniate:

$$As_2O_3 + Na_2CO_3 + 2NaNO_3 = Na_4As_2O_7 + N_2O_3 + CO_2,$$

and then pouring out while fused on a slab, and when cool boiling the residue with water:—

$$Na_4As_2O_7 + 15H_2O = 2(Na_2HAsO_4 7H_2O)$$

(the official crystallized salt).

Sodæ Arsenias, B.P., is in colourless transparent prisms soluble in water, the solution being alkaline. Heated to 300° it loses 40·38 per cent of its weight.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 105.)

The Pharmacopœial crystallized salt, though nominally containing $7H_2O$, is sometimes liable to be contaminated with a salt of 12 equivalents of water of crystallization, and consequently suffers a considerable deterioration in strength. Roughly speaking, the percentage of As would be reduced by the entire substitution of the latter for the former from 24 to 18·5. The difference in the amount of water in $Na_2HAsO_4.12H_2O$ and $Na_2HAsO_4.7H_2O$ is that

between 53·73 and 40·39 per cent. For this reason the official solution of disodium arseniate (*liquor sodæ arseniatis*) consists of four grains of the anhydrous Na_2HAsO_4 dissolved in an ounce of distilled water. The heat of 300° F. employed to dehydrate the crystals does not convert the residual salt into pyroarseniate, a temperature of 390° to 400° F. being required to effect this change.

TRIARGENTIC ARSENIATE (SYN. *Arseniate of Silver*). **Formula, Ag_3AsO_4.**

Is the chocolate precipitate produced by all soluble arseniates in argentic nitrate solution, or by the free acid in solutions of argent-ammonium nitrate, also during the volumetric estimation of disodium arseniate. It dissolves in excess of ammonium hydrate, and in acetic and nitric acids, whilst hydrochloric acid converts it into chloride. It is distinguished from argentic arsenite by its colour and by not leaving metallic silver when heated.

CALCIUM HYDROGEN-ARSENIATE. Formula, $CaHAsO_4$, and

BARIUM HYDROGEN-ARSENIATE. Formula, $BaHAsO_4$.

Are the white precipitates produced on adding calcium and barium chlorides respectively to disodium arseniate, the formation of which constitutes two of the B.P. tests for that body. As produced in this manner, they frequently contain more or less of the trimetallic salts. The former is found native, being contained in the minerals *pharmacolite* and *haidingerite*.

MAGNESIUM AMMONIUM ARSENIATE (SYN. *Ammonio Arseniate of Magnesia*). **Formula, $MgNH_4AsO_4$.**

Is formed in magnesian solutions by a mixture of a soluble arseniate and ammonium hydrate. Like magnesium ammonium phosphate, it is a white crystalline precipitate almost insoluble in a weak solution of ammonium hydrate, but dissolving in pure water slightly. When precipitated it contains $Mg(NH_4)AsO_4.6H_2O$, but by drying at 212° F. the formula becomes $2Mg(NH_4)AsO_4.H_2O$ (molecular weight, 380).

ZINC ARSENIATE. Formula, Zn_32AsO_4.

A white precipitate formed on adding zinc sulphate to disodium arseniate, according to the reaction stated in the B.P.

The decomposition is rather complex, being:—

$$4Na_2HAsO_4 + 4ZnSO_4 = Zn_32AsO_4 + ZnH_42AsO_4 + 4Na_2SO_4.$$

The latter salt is soluble, the former being that which falls as the precipitate. In the presence of a little ammonium or sodium hydrate, the whole is converted into the trimetallic salt, thus:—

$$2Na_2HAsO_4 + 3ZnSO_4 + 2NaHO = Zn_32AsO_4 + 3Na_2SO_4 + 2H_2O.$$

TRICUPRIC ARSENIATE (SYN. *Arseniate of Copper*). **Formula, Cu_32AsO_4.**

A green precipitate falling from a solution of cupric sulphate or cuprammonium sulphate upon the addition of a soluble arseniate. The reaction with the first salt and the ordinary disodium arseniate is the same as that with the latter body and zinc sulphate. In the case of the addition of cuprammonium sulphate no acid salt is formed, but if enough be added all the arseniate falls. There are six minerals in which cupric arseniate is contained, *euchroite* and *olivenite* being the most important.

TRIFERROUS ARSENIATE (Syn. *Ferri Arsenias*). **Formula, Fe_32AsO_4.**

Results from mixing a solution of ferrous sulphate with sodium acetate and disodium arseniate, washing the precipitate, and drying at a temperature not exceeding 100° Fahr. The reaction is:

$$3FeSO_4 + 2Na_2HAsO_4 + 2NaC_2H_3O_2 = Fe_32AsO_4 + 2HC_2H_3O_2 + 3Na_2SO_4.$$

In consequence of the loss of arseniate which would occur if a similar reaction to that represented under *zinc arseniate* were allowed to take place (viz., the formation of a soluble ferrous hydrogen-arseniate), sodium acetate is added to prevent such an action. It does this by giving up its sodium to the spare molecule of SO_4, and thus liberating acetic acid, in which the triferrous arseniate is not soluble. It has been stated that the addition of the acetate prevents the formation of free sulphuric acid, but such a reaction could never take place in the presence of a neutral arseniate. The real fact is doubtless, that it prevents the production of ferrous hydrogen-arseniate ($FeHAsO_4$?).

Ferri Arsenias is a tasteless amorphous powder of a green colour, insoluble in water, but readily dissolved by hydrochloric acid. Boiled with an excess of sodium hydrate, it is converted into ferroso-ferric hydrate, and sodium arseniate passes into solution.

When first precipitated, the salt is white; but by exposure to the air it becomes greenish, owing to the formation of ferric oxyarseniate.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 106.)

COMPOUNDS OF ARSENIC WITH THE HALOGENS.

ARSENIOUS CHLORIDE. Formula, $AsCl_3$.

Is produced (accompanied by a flash of light) when powdered arsenic is dropped into chlorine, and is usually prepared by distilling arsenious anhydride with strong hydrochloric acid. It is a colourless, volatile, and very poisonous liquid, which, in contact with water, forms arsenious and hydrochloric acids.

ARSENIOUS IODIDE. Formula, AsI_3.

Is a deep-red crystalline solid, produced by heating iodine with arsenic. A bromide and fluoride also exist, which are fluid.

COMPOUNDS OF ARSENIC WITH SULPHUR.

Arsenic unites with **sulphur** in three proportions, viz:—

ARSENIC DISULPHIDE (Syns. *Realgar. Red Sulphide of Arsenic. Red Orpiment*). **Formula, As_2S_2.**

This body exists in nature as crystalline prismatic masses of a red or orange colour, in many parts of Europe (Switzerland, Bohemia, etc.) and in North America. It burns with a blue flame, producing sulphurous anhydride and arsenious anhydride. When used for painting on distempered walls, it is said to evolve arsenical fumes. It may be prepared by heating arsenious anhydride or metallic arsenic with sulphur, in atomic proportions (75 of As and 32 of S).

When a salt analogous to ammonium sulphydrate is digested with arsenic disulphide, hyposulpharsenites are produced. The most easily prepared is :—

AMMONIUM HYPOSULPHARSENITE. **Formula, NH_4AsS_3.**

Which deposits in brown grains on keeping a neutral solution containing arsenic disulphide dissolved in ammonium sulphydrate in a closed vessel.

None of these salts are of pharmaceutical interest.

ARSENIOUS SULPHIDE (SYNS. *Yellow Sulphide of Arsenic. King's Yellow. Auripigmentum. Orpiment*). **Formula, As_2S_3.**

Is the precipitate formed by sulphuretted hydrogen in arsenious solutions. In nature it is found in translucent, yellow, cleavable prisms. It may be fused and volatilized at a high temperature without decomposition. The native article often contains more arsenic than the formula would indicate, and it is therefore a dangerous preparation which is rarely used.

It is insoluble in boiling solution of hydrogen-potassium tartrate and in hydrochloric acid.

When treated with cold potassium (or sodium) hydrate, an analogous decomposition occurs, as when antimonious sulphide is boiled with either of these substances, namely :—

$$4As_2S_3 + 10NaHO = \underset{\text{(Sodium meta-sulpharsenite.)}}{6Na(AsS_2)} + 2Na_2HAsO_3 + 4H_2O.$$

On adding an acid, however, the precipitate is pure arsenious sulphide, no sulphuretted hydrogen being evolved.

$$6Na(AsS_2) + 2Na_2HAsO_3 + 10HCl = 4As_2S_3 + 10NaCl + 6H_2O.$$

AMMONIUM SULPHARSENITE. **Formula, $(NH_4)_3AsS_3$.**

Is the body formed in the qualitative analysis of metals of the second group, when the precipitate caused by sulphuretted hydrogen is digested in ammonium sulphide. When sulphuretted hydrogen is passed into a solution containing *arsenic* acid or an *arseniate*, a precipitate does not form sometimes till after the lapse of some hours. This precipitate when formed is yellow, and answers when analyzed to the formula of As_2S_5. By treatment with carbon disulphide, however (or any other suitable solvent), an amount of sulphur is dissolved out, and As_2S_3 is left. We therefore consider that the As_2S_5 is not a truly definite arsenic sulphide, but only a mixture of arsenious sulphide and free sulphur

CHAPTER XIII.

HYDROCARBONS AND THEIR DERIVATIVES.

Formerly the substances which are treated of in this and the succeeding chapters were viewed as being the products of some mysterious influence called "vital force," and their study was therefore separated from that of the elements, and classed as *organic chemistry*. In 1828, however, Wöhler succeeded in making urea by simply heating ammonium cyanate; and subsequently it was discovered that potassium cyanide could be made by passing nitrogen over carbon and potassium hydrate heated to redness. This step gained, the absolute synthesis of urea from its elements, without the aid of "vital force," was quickly accomplished. Again, by passing the electric spark between carbon points in an atmosphere of hydrogen, acetylene, C_2H_2, was obtained :—

$$C_2 + H_2 = C_2H_2.$$

By acting on this compound with nascent hydrogen, we can get ethene, C_2H_4 :—

$$C_2H_2 + H_2 = C_2H_4.$$

When ethene is placed in contact with strong sulphuric acid, it forms ethyl sulphuric acid :—

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4.$$

Lastly, by acting on ethyl sulphuric acid with water, ordinary alcohol is formed :—

$$C_2H_5HSO_4 + H_2O = C_2H_5HO + H_2SO_4.$$

Thus we have another body hitherto only produced by fermentation, and the very existence of which was supposed to be due to vital force, made directly from purely inorganic constituents. In thus doing away with the term *organic body*, the student must note that the true *organized bodies*, such as animal and vegetable tissues, still remain a distinct group unproduceable without the aid of the vital force.

A marked property of many of these bodies is, that they are isomeric with each other, *i.e.*, having a similar percentage composition, but differing in properties. Isomeric bodies (ἴσος, equal; μέρος, part) may be in turn classified as follows :—

1. **Truly isomeric**: this name is given to bodies which, differing only in *physical properties*, undergo exactly similar decompositions when submitted to the action of other bodies or of heat. EXAMPLES: the volatile oils of lemon and of turpentine.

2. **Metameric bodies** (μετὰ, beyond; a changed condition) are those which, while they are alike in percentage composition and molecular weight, yet undergo different decompositions by the action of reagents.

3. **Polymeric bodies** are those which, although differing in molecular weight, have an analogous percentage composition This is most characteristic of a certain series of hydrocarbons which are all polymeric (πολύς, many ; μέρος, part) with methene, CH_2.

In order to see the beautiful regularity and simplicity of the compounds of carbon and hydrogen, we must first glance at,—

I. Homologous and Isologous Series of Hydrocarbons.

It has been already shown (see page 136) that the atom of carbon can form an endless variety of compounds, commencing with CH_4 and increasing by a constant addition of CH_2, and that such a series is called homologous, and each series is represented by a typical formula. The ordinary saturated series, having the formula C_nH_{2n+2}, can lose a molecule of hydrogen, and so give birth to another series having the formula C_nH_{2n}. This giving up of hydrogen may be carried on through many more degrees; but the following table shows the chief series thus constituted.

The nomenclature is obtained by uniting a prefix of "meth, eth," etc., which indicates the number of carbon atoms, and an affix of "ane, ene, ine," etc., which indicates the series, thus :—

Typical Formula.		-ane. C_nH_{2n+2}	-ene. C_nH_{2n}	-ine. C_nH_{2n-2}	-one. C_nH_{2n-4}	-une. C_nH_{2n-6}
Meth-	C	CH_4	CH_2	—	—	—
Eth-	C_2	C_2H_6	C_2H_4	C_2H_2	—	—
Prop-	C_3	C_3H_8	C_3H_6	C_3H_4	C_3H_2	—
But-	C_4	C_4H_{10}	C_4H_8	C_4H_6	C_4H_4	C_4H_2
Pent-	C_5	C_5H_{12}	C_5H_{10}	C_5H_8	C_5H_6	C_5H_4
Hex-	C_6	C_6H_{14}	C_6H_{12}	C_6H_{10}	C_6H_8	C_6H_6
and so on by the Greek numerals.		etc.	etc.	etc.	etc.	etc.

For example, the formula of ethane being wanted, we consider that *eth* = C_2 and *ane* = C_nH_{2n+2}; therefore C_2 and H twice two, viz. four, and two added = H_6: ergo the formula of ethane is C_2H_6. By diligently studying and mastering this nomenclature, the formulation of any body is made perfectly simple. Running down the table, we have the *homologous* series, differing by CH_2; and running across, we have the *isologous* series, differing by H_2.

All members of these series are hydrocarbons of *even* atomicity, derived from *saturated molecules* by the abstraction of one or more *molecules* of hydrogen (pairs of hydrogen atoms). They are all capable of existing in the free state, and are known by special names, such as paraffins, olefines, etc., as hereafter described.

II. Unsaturated Hydrocarbon Radicals (*basylous*).

Each saturated hydrocarbon, moreover, besides possessing the power of giving up H_2 to form other hydrocarbons capable of free existence, can also part with single atoms of H, thus producing compounds of uneven atomicity, which do not exist in the free state without duplication, and behave as **basylous radicals.** These radicals are named by adding *yl* to the name of the even hydrocarbon from which they are derived, except the monad series in which the final *ane* is converted into *yl.*

Taking a table of the full possible hydrocarbons thus obtainable, with the prefixes and affixes as above, we have :—

TYPICAL FORMULÆ OF HYDROCARBONS.

	Saturated. -ane C_nH_{2n+2}	*Monads.* -yl C_nH_{2n+1}	*Dyads.* -ene C_nH_{2n}	*Triads.* -enyl C_nH_{2n-1}	*Tetrads.* -ine C_nH_{2n-2}	*Pentads.* -inyl C_nH_{2n-3}	*Hexads.* -one C_nH_{2n-4}	*Heptads.* -onyl C_nH_{2n-5}
Meth-	CH_4	$(CH_3)'$	$(CH_2)''$	$(CH)'''$	—	—	—	—
Eth-	C_2H_6	$(C_2H_5)'$	$(C_2H_4)''$	$(C_2H_3)'''$	$(C_2H_2)^{iv}$	$(C_2H)^{v}$	—	—
Prop-	C_3H_8	$(C_3H_7)'$	$(C_3H_6)''$	$(C_3H_5)'''$	$(C_3H_4)^{iv}$	$(C_3H_3)^{v}$	$(C_3H_2)^{vi}$	$(C_3H)^{vii}$
But-	C_4H_{10}	$(C_4H_9)'$	$(C_4H_8)''$	$(C_4H_7)'''$	$(C_4H_6)^{iv}$	$(C_4H_5)^{v}$	$(C_4H_4)^{vi}$	$(C_4H_3)^{vii}$
Pent-	C_5H_{12}	$(C_5H_{11})'$	$(C_5H_{10})''$	$(C_5H_9)'''$	$(C_5H_8)^{iv}$	$(C_5H_7)^{v}$	etc.	etc.
Hex-	C_6H_{14}	$(C_6H_{13})'$	$(C_6H_{12})''$	$(C_6H_{11})'''$	$(C_6H_{10})^{iv}$	$(C_6H_9)^{v}$	—	—
Etc.	etc.	etc.	etc.	etc.	etc.	etc.	—	—

By carefully connecting in the mind the **prefix** to indicate the **number of carbon atoms**, and the **affix** to indicate the **atomicity** and **typical formula**, any radical may be at once formulated from the above table.

The radicals all behave like metals, and form salts by displacement of the **hydrogen** of acids. Their chlorides, bromides, or iodides are called **haloid ethers**, their oxides **simple ethers**, their hydrates **alcohols**, their salts with

oxygenated acids, **compound ethers**, and their hydrides are the corresponding *hydrocarbons*. For example, taking the monad radical ethyl, we have—

Haloid ether . . .	$(C_2H_5)'I'$, *ethyl iodide*.
Simple ether . . .	$(C_2H_5)_2'O$, *ethyl oxide* (*ether*, B.P.).
Alcohol	C_2H_5HO, *common alcohol*.
Compound ether . .	$C_2H_5.C_2H_3O_2$, *ethyl acetate* (*acetic ether*, B.P.).
Hydride	$C_2H_5.H$, *ethane*.

These basylous radicals can also displace more or less completely the hydrogen of ammonia to form **amines**;

Example,—

$$\textit{Ethylamine}, \ NH_2(C_2H_5)', \text{ or } N\begin{cases}(C_2H_5)'\\ H\\ H\end{cases}$$

When the hydrogen of ammonia is entirely displaced by a triad radical, the resulting compound is called a **nitril**. The *cyanides* of the monad series may be viewed as being the *nitrils* of the triad radical *immediately above in number of carbons*, thus:

Methyl cyanide, $(CH_3)'CN = (C_2H_3)'''N$, *ethenyl nitril*.
Ethyl cyanide $(C_2H_5)'CN = (C_3H_5)'''N$, *propenyl nitril*.

It is by this means that we can pass from any one series to that immediately above it in complexity of carbon.

The basylous radicals can unite with metals to form saturated compounds, capable of free existence, and called **organo-metallic** bodies,

Example,—

Zinc ethyl . . . $(C_2H_5)_2'Zn''$.

Lastly, they can replace part or the whole of the hydrogen of phosphuretted, arseniuretted, and antimoniuretted hydrogen, to form bodies called respectively **phosphines, arsines, and stibines**, thus—

Triethyl Phosphine, $P'''(C_2H_5)_3'$.
Triethyl Stibine, $Sb'''(C_2H_5)_3'$.

III. Oxygenated Hydrocarbon Radicals (*acid*).

Each of the above-mentioned monad basylous radicals can exchange two atoms of their hydrogen for one of oxygen, and so give birth to a corresponding oxygenated radical, which is also a monad. These latter have been called *acid radicals*, but somewhat unfortunately, because it is apt to cause confusion with the ordinary *acidulous* radicals, with which they have no identity; and the term oxygenated radical is therefore better. The new radicals thus formed are terminated in yl; and they are called, not after the name of the basylous radical from which they are derived, but by prefixing a portion of the name of the acid to which they give birth, as will shortly be shown. Examples of such radicals are found in the following:—

Methyl $(CH_3)'$	gives	birth to	$(CHO)'$ *formyl*.
Ethyl $(C_2H_5)'$	,,	,,	$(C_2H_3O)'$ *acetyl*.
Propyl $(C_3H_7)'$	,,	,,	$(C_3H_5O)'$ *propionyl*.
Butyl $(C_4H_9)'$	,,	,,	$(C_4H_7O)'$ *butyryl*.
Pentyl $(C_5H_{11})'$	,,	,,	$(C_5H_9O)'$ *valeryl*.

Dyad basylous radicals can suffer two successive steps of oxidation, and thus produce two oxygenated radicals. For example,—

Ethene C_2H_4 by the 1st oxidation forms C_2H_2O, *glycollyl*.
,, C_2H_4 ,, 2nd ,, ,, C_2O_2, *oxalyl*.

The resulting oxygenated radicals are in this case dyads, following the atomicity of the basylous radicals from which they spring. The **haloid salts** of the oxygenated radicals are called **acid halides**, their *hydrides* are termed **aldehyds**, their *oxides*, **anhydrides** or **anhydrous acids**, and their *hydrates* are called **acids**. Thus we have :—

Acetyl Chloride $C_2H_3O.Cl$, *acetic chlor-anhydride.*
Acetyl Hydride $C_2H_3O.H$, *acetic aldehyd.*
Acetyl Oxide $(C_2H_3O)_2'O'$, *acetic anhydride* (*anhydrous acetic acid*).
Acetyl Hydrate $C_2H_3O.HO$, *acetic acid* (usually written $HC_2H_3O_2$).

Like the corresponding basylous radicals, the oxygenated ones under consideration can displace the hydrogen of ammonia; but in this case the resulting compound is called an **amide**. Example :—

$$N\left\{\begin{matrix}(C_2H_3O)' \\ H \\ H\end{matrix}\right\} \textit{acetamide.}$$

Lastly, the oxygenated radical can combine with the basylous radical immediately below it in number of carbon atoms, to form a **ketone**. Example :—

$CH_3.C_2H_3O$, *acetone.*

IV. Hydrocarbons on the Type C_nH_{2n+2} or, Paraffins.

The members of this series are called **paraffins**, because many of them are found in the illuminating oils sold as *petroleum* or *paraffin*. These oils are chiefly obtained from North America, where they rise from the earth like ordinary water springs, and are considered to be produced by the slow decay of vegetable substances deeply imbedded in the earth. Certain varieties of cannel coal and a peculiar mineral obtained at Boghead, in Scotland, yield paraffin oil by destructive distillation.

The series is a long one, commencing with methane or marsh gas, CH_4, already described at page 138, and increasing in complexity by a regular addition of CH_2. The lower members are :—

Methane	CH_4.
Ethane	C_2H_6.
Propane	C_3H_8.
Butane	C_4H_{10}.

All of which are gaseous at ordinary temperatures. Next we have a series commencing with pentane, C_5H_{12}, and ending with $C_{14}H_{30}$, which are liquids boiling at points varying from 90° to 500° F., while in some of the heavier American oils we meet with still more complex paraffins boiling above 600° F. and solid at ordinary temperatures.

All these paraffins, when subjected to the action of monad metalloids, give up the whole or a part of their hydrogen in exchange for the metalloid, forming salts of new radicals; thus marsh gas, CH_4, can by successive steps be changed by the action of chlorine (in sunlight) into :—

CH_3Cl	Methyl Chloride.
CH_2Cl_2	Methene Chloride.
$CHCl_3$	Methenyl Chloride.
CCl_4	Carbon Tetrachloride.

The paraffins may be produced artificially by heating metallic zinc and

water in a sealed tube with the iodides of their corresponding basylous radicals.

Example: ethyl iodide, thus treated, yields ethane.

$$2C_2H_5I + 2H_2O + Zn_2 = 2C_2H_6 + ZnI_2 + Zn2HO.$$

The following is a full list of the **paraffins** actually discovered:—

Name.	Formula.	Boiling Point, Fah.	Name.	Formula.	Boiling Point, Fah.
Methane	CH_4	—	Nonane	C_9H_{20}	298·4°
Ethan	C_2H_6	—	Decane	$C_{10}H_{22}$	334·4°
Propane	C_3H_8	—	Undecane	$C_{11}H_{24}$	363·2°
Butane	C_4H_{10}	33·8°	Dodecane	$C_{12}H_{26}$	395·6°
Pentane	C_5H_{12}	100·4°	Tridecane	$C_{13}H_{28}$	424·4°
Hexane	C_6H_{14}	158·0°	Tetradecane	$C_{14}H_{30}$	464·0°
Heptane	C_7H_{16}	210·2°	Pentadecane	$C_{15}H_{32}$	505·6°
Octane	C_8H_{18}	255·2°	Hexdecane	$C_{16}H_{34}$	532·4°

The more volatile liquid compounds of the paraffin series are now extensively used for lighting purposes. They are known in commerce as petroleum spirit, gazoline, or benzoline, and give off highly inflammable vapours at the ordinary temperature. They require to be burned in special lamps, while their sale is restricted by Act of Parliament to certain hours of the day. The less volatile, which will not take fire on the application of a lighted match, and burn continuously at a temperature below 100° F., may be burned in lamps of ordinary construction and retailed at all hours of the day. The more viscid members of the series are greatly used as lubricating oils, while the solid ones constitute what is known as paraffin wax.

The paraffins are distinguished by their great chemical indifference (*parum affinis*). Being saturated hydrocarbons, they are incapable of uniting directly with monatomic elements or radicals, and are not sensibly affected by cold sulphuric acid. Nitric acid does not affect the lower paraffins; and their nitryl compounds, called nitroparaffins, have to be formed by indirect means. The higher members, however, are attacked and form nitro compounds.

V. Hydrocarbons on the Type C_nH_{2n}.

These hydrocarbons are termed **olefines**. The series probably commences with **methene**, CH_2, as yet, however, unisolated, and proceeds up as far as **melene**, $C_{30}H_{60}$, which is, at ordinary temperatures, a solid. The most interesting compound of this class (because it is a leading constituent of coal gas) is **ethene** (*olefiant gas*) C_2H_4, already mentioned at page 138; and its production by the subtraction of the elements of water from alcohol is characteristic of the whole series, the members of which may be obtained by a similar process from the hydrate of the monad basylous radical having a similar number of carbon atoms. All the olefines themselves act as dyad basylous radicals.

The **olefines** are prepared,—

1. By the decomposition of paraffins at the moment of their liberation

from their compounds by the action of zinc or sodium. Thus, by heating ethyl iodide with zinc, we form tetrane:—

$$2C_2H_5I + Zn = C_4H_{10} + ZnI_2.$$

but at the moment of liberation the tetrane breaks up into ethane and ethene, thus:—

$$2C_2H_5I + Zn = C_2H_6 + C_2H_4 + ZnI_2.$$

2. By the abstraction of water from the alcohol of the corresponding monad radical. Thus, ethyl alcohol, heated with strong sulphuric acid, forms *ethene*:—

$$C_2H_5HO + H_2SO_4 = C_2H_4 + H_2SO_4.H_2O.$$

3. By heating a haloid ether (preferably a bromide) of the corresponding monad radical with alcoholic potassium hydrate. Thus, ethyl bromide, so treated, yields *ethene*:—

$$C_2H_5Br + KHO = C_2H_4 + KBr + H_2O.$$

Many other methods are known, which may be found in larger manuals.

The members of this series all unite directly with chlorine, bromine, and iodine, forming haloid ethers. Example:—

$$C_2H_4'' + Cl_2 = C_2H_4Cl_2;$$

which haloid ethers, treated with argentic acetate, give rise to diatomic acetic ethers:—

$$C_2H_4Br_2 + 2AgC_2H_3O_2 = 2AgBr + C_2H_4.2C_2H_3O_2;$$

and these ethers, distilled with a caustic alkali, yield diatomic alcohols or glycols:—

$$C_2H_4.2C_2H_3O_2 + 2KHO = C_2H_4.2HO + 2KC_2H_3O_2.$$

Some olefines are capable of uniting with concentrated sulphuric acid when briskly shaken up with it, forming acid ethers which contain the corresponding monad alcohol radical to the olefines employed; thus ethene is absorbed by sulphuric acid, forming ethyl-sulphuric acid:—

$$C_2H_4 + H_2SO_4 = C_2H_5.HSO_4.$$

These acid ethers distilled with water re-form sulphuric acid and the monatomic alcohol analogous to the olefine. Thus:—

$$C_2H_5HSO_4 + H_2O = C_2H_5HO + H_2SO_4.$$

List of the Normal Olefines:—

Name		Formula.	Boiling Point, F.
Ethene	or ethylene	C_2H_4	Gaseous.
Propene	,, propylene	C_3H_6	,,
Tetrene	,, butylene	C_4H_8	33·8°
Pentene	,, amylene	C_5H_{10}	95·0
Hexene	,, hexylene	C_6H_{12}	149·0
Heptene	,, œnanthylene	C_7H_{14}	204·8
Octene	,, caprylene	C_8H_{16}	248·0
Nonene	,, nonylene	C_9H_{18}	284·0
Decene	,, paramylene	$C_{10}H_{20}$	320·0
Hexdecene	,, cetene	$C_{16}H_{32}$	527·0
Cerotene		$C_{27}H_{54}$	Solid, melts at 135°
Melene	,, melissene	$C_{30}H_{60}$	,, ,, ,, 144°

VII. Hydrocarbons on the Type C_nH_{2n-6}.

This is called the **Aromatic Series**, and the typical compound with which it commences is—

BENZENE (SYNS. *Benzol. Phenylhydride*). **Formula, C_6H_6.**

This body may be prepared by the action of heat upon acetylene :—

$$3C_2H_2 = C_6H_6,$$

or by heating benzoic acid with calcium hydrate :—

$$HC_7H_5O_2 + Ca2HO = C_6H_6 + CaCO_3 + H_2O.$$

In practice it is prepared by fractional distillation from coal-tar, being found in the portion distilling below 180° F.

Benzene is a colourless and highly refractive liquid, boiling at 177° F. It is very inflammable, and has been used as a cheap solvent for fats, resins, sulphur, and phosphorus. It is insoluble in water, but miscible with alcohol and ether, and has a specific gravity of ·899 at 32° F.

It is much employed for the manufacture of—

NITRO-BENZENE (SYNS. *Nitrobenzol. Oil of Myrbane*). **Formula, $C_6H_5NO_2$.**

When purified benzene is treated with a mixture of fuming nitric acid and a little sulphuric acid, the nitro-benzene separates as a yellow oil, having a strong odour of bitter almonds. If the acids be allowed to act too long, or the mixture get too hot, a dinitro benzene, $C_6H_4(NO_2)_2$, would be produced, which crystallizes in long yellow needles. Nitro benzene is much sold as *artificial essence of bitter almonds*, and is even used to adulterate the real oil. This adulteration is readily detected by the property which it possesses of becoming changed into aniline by the action of reducing agents. The best test to employ is nascent hydrogen, evolved from a mixture of zinc and dilute sulphuric acid. The resulting reaction is as follows :—

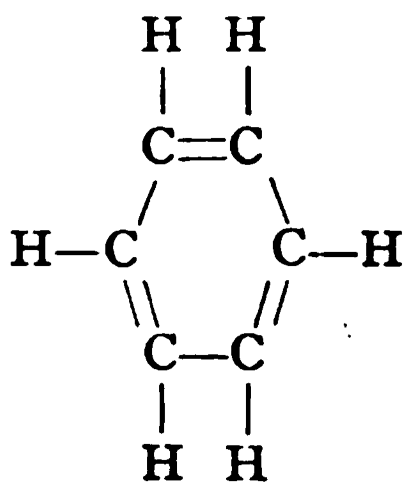
$$C_6H_5NO_2 + 3H_2 = C_6H_7N + 2H_2O.$$

In practice the oil is dissolved in a little alcohol, and added to a tube containing zinc and dilute sulphuric acid. After standing for some time, a fragment of potassium chlorate is added, which immediately develops a beautiful mauve colour, caused by the oxidation of the aniline. Many chemists prefer to use a little solution of *chlorinated lime*, to develop the colour, instead of potassium chlorate. This is a process which every student should try for himself upon oil of myrbane, because much of its success depends on the degree of dilution of the sulphuric acid and upon the quantity of potassium chlorate employed—matters best learnt by experience.

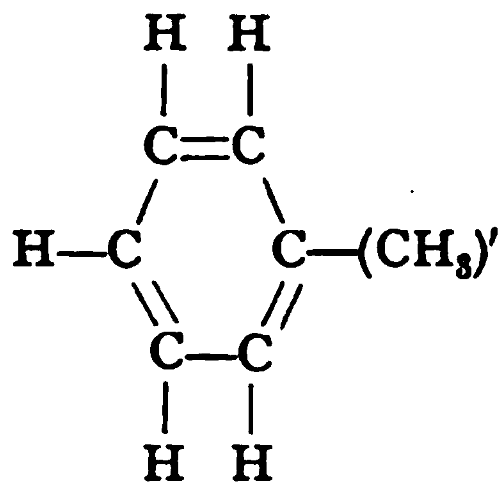
The quantitative estimation is somewhat uncertain, but the following process yields at least nine-tenths of the adulteration in a state fit for weighing. 100 grains of essence of bitter almonds are agitated in a wide-mouthed flask with 300 to 400 grain measures of saturated solution of sodium hydrogen-sulphite, and then the whole treated with a little ether. The solution is quickly filtered, evaporated to dryness, and the residue of nitro-benzene is weighed.

The whole members of the aromatic group and their derivatives are of the greatest interest as being of late years chiefly extracted from coal tar, and utilized in almost innumerable ways, although till but recently either entirely unknown or considered to be waste products. From modifications of this group by substitution of various radicals for portions of the hydrogen of its members, we have carbolic, benzoic, cinnamic, and other acids; aniline and similar dyes, nitrobenzene, turpentine, resins, and the great bulk of our essential oils.

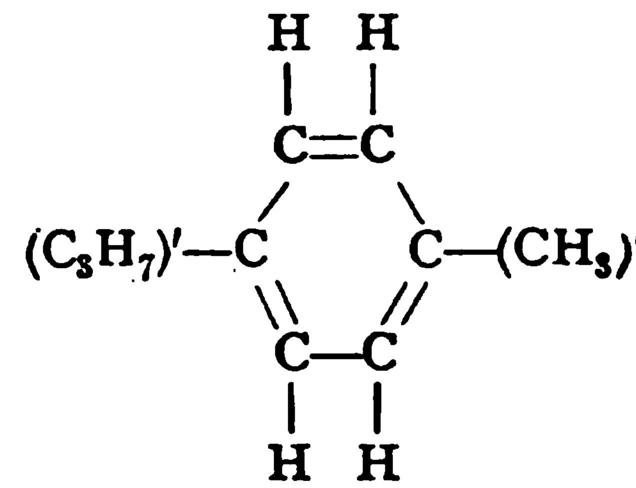
A most curious fact is, that all the members of the aromatic group may be viewed as derived from the great typical hydrocarbon **benzene**, by substitution of various radicals for portions of its molecule. Thus, the next member, **toluene**, C_7H_8, may be viewed as being really methyl-benzene, $C_6H_5(CH_3)$. It is unfortunately impossible, within the limits set to the present edition, to go thoroughly into these relations; but one more example may be given to show how turpentine, $C_{10}H_{16}$, may be theoretically connected with benzene, and to give an idea of the immense depth of research which has been brought to bear upon the aromatic group. Turpentine is first viewed as cymene hydride, $H_2C_{10}H_{14}$. In turn cymene, $(C_{10}H_{14})$, is itself regarded as being methyl-propyl-benzene $(C_6H_4.CH_3.C_3H_7)$, that is, benzene, C_6H_6, in which two hydrogens have been respectively replaced by the monad radicals methyl and propyl. The constitution of these compounds may be thus represented,—



Benzene,
C_6H_6.



Toluene, or
Methyl-benzene,
C_7H_8.



Cymene, or
Methyl-propyl-benzene,
$C_{10}H_{14}$.

It is easy to see that bodies so constituted may have an immense amount of isomerism, as indeed they have; but the study of them is quite beyond the scope of the present work: it must suffice to give a glance only at those members of the series of actual interest in pharmacy or medicine.

CYMENE. Formula, $C_{10}H_{14}$.

Is known in two metameric varieties, one of which is found among the lighter oils separable from coal tar by fractional distillation, while the other exists in the oil of *Cicuta virosa*. This modification may also be obtained from oil of *cumin* (cumic aldehyd, $C_{10}H_{12}O$), by the action of alcoholic potash.

CINNAMEIN. Formula, C_8H_8.

Is a colourless oil existing in *storax*, and easily obtainable by distilling the storax with water and an alkali to fix the cinnamic acid. By heating in a sealed tube to 400° F., it is converted into a white solid called **metacinnamein.**

NAPHTHALENE. Formula, $C_{10}H_8$.

Is a white solid separable from coal tar by fractional distillation, which is interesting as being the source of artificial benzoic acid. (*See* **Benzoic Acid.**)

ANTHRACENE. Formula, $C_{14}H_{10}$.

Is found in commerce as a yellow softish mass distilled from coal tar. It is used for lubricating delicate machinery, and also as a source of **alizarin,** a red colouring matter used in dyeing, and formerly only obtainable from **madder.**

In explaining this reaction it should be noted that all the hydrocarbons of the series possess the power of forming by oxidation peculiar bodies called *quinones*, in which H_2 is displaced by the group O_2 acting as a dyad, exactly as Hg_2 has already been seen to act in mercurous ammonium chloride. They are neutral bodies, and by the action of nascent hydrogen yield *hydroquinones*, that is, where the place of H_2 has been taken by $(HO)_2$ in the hydrocarbon. Examples of this may be seen by comparing :—

C_6H_6	$C_6H_4(O_2)''$	$C_6H_4(HO)_2'$
Benzene.	Quinone.	Hydroquinone.

If therefore anthracene be heated with potassium dichromate and sulphuric acid, we obtain anthraquinone

$$C_{14}H_{10} + O_3 = C_{14}H_8(O_2)'' + H_2O.$$

From this body, by heating with bromine, we obtain a substitution product called dibrom-anthraquinone :—

$$C_{14}H_8(O_2)'' + 2Br_2 = C_{14}H_6Br_2O_2 + 2HBr.$$

This product, fused with potassium hydrate at 350° F., yields the potassium compound of alizarin :—

$$C_{14}H_6Br_2(O_2)'' + 4KHO = C_{14}H_6(KO)_2'(O_2)'' + 2KBr + 2H_2O.$$

On dissolving the product in water and acidulating, the crude alizarin is precipitated and purified by sublimation. Alizarin is therefore anthraquinone in which an additional group of H_2 has been displaced by $(HO)_2$ thus :—

$$C_{14}H_6(HO)_2'(O_2)''.$$

VIII. Terpenes. General Formula, $C_{10}H_{16}$.

An immense number of these bodies are isomeric with each other, and exist in many volatile oils. They are prone to oxidation, and therefore the essential oils of commerce usually are partially altered, and when distilled carefully or refrigerated they are found to consist of—

1. An **elæopten**, which is the more volatile and unchanged portion, remaining perfectly fluid, and usually isomeric with oil of turpentine, $C_{10}H_{16}$.

2. A **stearopten**, which is the portion frequently crystallizing out, which has undergone alteration by oxidation or contact with moisture. The body is frequently isomeric with common camphor, $C_{10}H_{16}O$.

Oleum terebinthinæ is the volatile oil distilled from the natural crude turpentine, an oleo-resin obtained from the pine tribe of coniferous plants. It is described by the B.P. as being limpid, colourless, with a strong peculiar odour and pungent bitter taste. The natural turpentine which exudes from the tree, when submitted to distillation, yields a distillate of common oil of turpentine, the residue in the retort being the well known article resin (*resina*, B.P.). If this common oil be distilled with potassium carbonate *in vacuo*, the pure oleum terebinthinæ, known in commerce as *rectified spirit of turpentine*, is obtained. When thus purified, it consists of one of two isomeric hydrocarbons, according to the source of the original oleo-resin. The English oil, distilled from American turpentine, is called chemically *anstraterebenthene*, and the French oil, from *Pinus maritima*, is termed *terebenthene*. Both of these terpenes have the formula, $C_{10}H_{16}$, together with a specific gravity of ·864 and boil at 320° F. The former, however, exhibits a dextro- and the latter a lævo- gyrate action on polarized light. Turpentine oils undergo a great variety of decomposition by the action of heat and reagents. A paper steeped in the ordinary oil and then introduced into chlorine, absorbs the latter so violently as to burst into flame. By passing dry hydrochloric acid gas into oleum terebinthinæ

a crystalline compound called **terebenthene hydrochlorate**, $C_{10}H_{16}HCl$, is obtained, and was formerly sold as *artificial camphor*. When ordinary turpentine oil is exposed to the action of water, it unites with it and deposits crystals of **terpin hydrate**, $C_{10}H_{16}3H_2O$. By drying at 212° F. these lose water, and are converted into **terpin**, $C_{10}H_{16}2H_2O$. In addition to these hydrates the following are known, viz., **terpentin hydrate**, $C_{10}H_{16}H_2O$, and **terpinol**, $(C_{10}H_{16})_2H_2O$.

Oil of turpentine is insoluble in water, but miscible with strong alcohol, carbon disulphide, and ether. It is a good solvent of oils, resins, phosphorus, sulphur, and many other substances. It is employed in the laboratory for taking the specific gravity of sugar and similar bodies which are soluble in water but insoluble in turpentine. It is powerfully acted on by nitric acid, potassium permanganate, and the other leading oxidants.

CAMPHOR (SYNS. *Camphoric Aldehyd. Camphoryl Hydride*)
Formula, $C_{10}H_{16}O$.

Is the type of the oxidized hydrocarbons (*stearoptens*) of the essential oils, and as such is best studied here.

Camphor is obtained from the bark and wood of the *Laurus Camphora*, or *Camphora officinarum*, from which it derives its name.

The Chinese mode of extraction is to boil the wood, cut into pieces of suitable size, in a vessel having a conical clay condenser inverted over it. The camphor sublimes into this clay vessel, which is lined with rice straw to prevent contamination of the sublimate by earthy matters.

The crude camphor imported from China is grey; that introduced from Japan (sometimes termed Dutch camphor) is pink. It invariably undergoes a second sublimation after it is brought to Europe before being used, and is then white, translucent, tough, and crystalline; has a powerful penetrating odour, and a pungent taste followed by a sensation of cold; floats on water; volatilizes slowly at ordinary temperatures; is slightly soluble in water, but readily soluble in rectified spirit and in ether; sublimes entirely when heated, and burns in the air with a smoky flame.

It is only slightly volatile at temperatures below 347° F., but above that degree it melts, and commences to boil at 400° F. It is soluble in water to the extent of one-tenth per cent. When an attempt is made to reduce it to powder, it does not succeed without the addition of some strong spirit. The temperature at which its specific gravity is taken affects the result greatly, causing it to vary from ·9862 to ·9958. When fragments of camphor are placed on water they assume a state of rapid movement. These movements are supposed by some to be attributable to the vapour evolved by the camphor preventing contact with the water; but it seems hardly probable that this would have sufficient power to move such large fragments as are thus caused to revolve. The fact, however, that a minute quantity of oil arrests the motion seems to lend some countenance to this opinion, as the vapour of camphor would be soluble in oil. The specific gravity of camphor at the freezing point has been found to be higher than that of water. At the degree of the greatest density of water (39·2° F.) it is also incapable of floating on that liquid, provided it has been made damp. An alcoholic solution is precipitated by water, and this is sometimes the method adopted for preparing an aqueous solution, as the camphor thus (in consequence of its finely-divided state) dissolves in the water much more readily than if introduced in the ordinary manner.

A stable liquid preparation may be made by adding a concentrated alcoholic solution of camphor to proof spirit in requisite proportions.

Ether, acetic acid, essential and fixed oils, liquid acids, chloroform, and

carbon disulphide are all good solvents of camphor. An alcoholic solution will take up much more mercuric chloride than alcohol alone. By the action of potassium permanganate or nitric acid, camphoric acid, $C_{10}H_{16}O_4$, is formed.

Camphor, though frequently represented as an aldehyd, does not strictly speaking belong to that class of bodies, as it does not combine with hydrogen sodium sulphite, nor does it form the corresponding alcohol (camphol) by the action of nascent hydrogen, these two reactions being regarded as essentially characteristic of true aldehyds. Unlike many similar bodies, it does not yield a resinous substance on oxidation either by nitric acid or the atmosphere. When distilled with phosphoric anhydride, it yields cymene. There is a substance termed "artificial camphor," which is occasionally substituted for, or used to adulterate, true camphor. It is produced by the action of hydrochloric acid on turpentine, melts at 240° F., and boils at 330° F. It is readily distinguished by inflaming it, then blowing out the flame, when the vapours which come off for a few seconds will have the odour of turpentine. By passing the products of its combustion into a solution of argentic nitrate, a precipitate of argentic chloride will result, to which the usual confirmatory tests may be applied. The gases formed by the burning of ordinary camphor will cause no precipitate. The artificial variety burns with a greenish colour, while the natural product gives a white flame. Both flames evolve carbon, and the vapours produced are consequently thick and sooty. Ordinary camphor is dextro-rotatory as regards polarized light. Some official volatile oils, viz. *oleum rosmarini* and *oleum lavandulæ*, contain a substance possessing the same chemical properties as camphor, but are inactive in the polariscope. A lævo-rotatory variety exists in the essential oil of feverfew.

Ngai camphor has for its chief source the *Blumea balsamifera*, D.C. It is isomeric with Borneo camphor, but differs in some physical characteristics.

Oleum anethi, obtained from the fruit of *Anethum graveolens* by distillation with water. It is described as pale yellow, with a pungent, acrid, but sweetish taste. It varies in specific gravity from ·88 to ·95, according to its age, and boils at about 375° F.

Oleum anisi, obtained as above from *Pimpinella anisum* or *Illicium anisatum* (star-anise). According to the B.P. it is,—

Colourless or pale yellow; with the odour of anise, and a warm sweetish taste. Concretes at 50°.

It consists of a terpene, $C_{10}H_{16}$, and a stearopten, $C_{10}H_{12}O$, which latter causes the concretion when cooled. Its specific gravity is from ·97 to ·99, and it absorbs oxygen by exposure, losing its property of concretion by cold. The stearopten is usually called anise camphor; and when acted on by antimonious chloride it thickens to a reddish matter, which deposits a white substance called *anisoin* on boiling with water. By oxidation with potassium dichromate and sulphuric acid, oil of anise yields a mixture of acetic and anisic acid ($C_8H_8O_3$).

Oleum anthemidis, distilled as above from the flower heads of *Anthemis nobilis*. It is described by the B.P. as being,—

Pale blue or greenish-blue, but gradually becoming yellow; with the peculiar odour and aromatic taste of the flowers. Great beauty characterizes the blue colour of the oil of chamomile when recently distilled.

It contains a terpene, $C_{10}H_{16}$, and also angelic aldehyd, C_5H_8O, which by heating with potassium hydrate yields potassium angelate:—

$$C_5H_8O + KHO = KC_5H_7O_2 + H_2.$$

Oleum cajeputi is distilled from the leaves of *Melaleuca minor*. It is imported from Singapore, and is described by the B.P. as being,—

Very mobile, transparent, of a fine pale bluish-green colour. It has a strong agreeable odour, and a warm aromatic taste, and leaves a sensation of coldness in the mouth.

The specific gravity of cajeput oil is about ·926. It consists chiefly of the monohydrate of a terpene called **cajeputene**, and its formula may therefore be taken as $C_{10}H_{16}H_2O$. It leaves on distillation a green resin soluble in ether.

Oleum carui is distilled from the fruit of *Carum Carui*, and is described in the B.P. as being colourless or pale yellow, odour aromatic, and taste spicy. It is a mixture of a true terpene (**carvene**, $C_{10}H_{16}$) and an oxidized portion (**carvol**, $C_{10}H_{14}O$). The latter may be separated from the former by agitation with ammonium sulphide, in which it dissolves, forming carvol sulphydrate $(C_{10}H_{14}O)_2H_2S$.

Oleum caryophylli is distilled from the unexpanded flower-buds of *Caryophyllus aromaticus*. According to the B.P. it is :—

Colourless when recent, but gradually becoming red-brown, having the odour of cloves and a pungent spicy taste. Sinks in water.

Chemically, this oil consists of a terpene, with eugenic acid, $HC_{10}H_{11}O_2$, and a stearopten called eugenin, probably isomeric with the acid. On distilling the oil with water the latter body may be observed to crystallize from the aqueous solution, while the eugenic acid may be separated as potassium hydrogen-eugenate, $KH2C_{10}H_{11}O_2 + Aq$, by agitation with weak warm solution of potassium hydrate and crystallizing.

Oleum cinnamomi. (*See* **Cinnamic Aldehyd.**)

Oleum copaibæ is distilled from the peculiar *oleo-resin* obtained from *Copaifera multijuga*. It is described in the B.P. as being colourless or pale yellow, with the odour and taste of copaiva.

It consists chiefly of a terpene *polymeric* with turpentine oil, and therefore has the formula of $C_{20}H_{32}$.

When the oleo-resin itself (*commonly called balsam of copaiba*) is examined, it is found to vary much in its constitution according to its source, for according to Flückiger, balsam from Maracaibo rotates a polarized ray to the right, and that from Maranha exhibits a left-handed polarization. It contains the volatile oil above described, and also two resins,—one (in quantities varying up to 60 per cent.) called **copaivic acid**, and another in small quantities (usually 2 per cent.), which is not acidulous. **Copaivic acid**, $HC_{30}H_{29}O_2$, is the portion of the copaiba which causes it to harden when mixed with magnesium or calcium oxides. The copaiba contains a little moisture; and in the presence of this, the oxides, being converted into hydrates, attack the resinous copaivic acid, forming magnesium or calcium copaivates, which crystallize and take up the oily portion, and the whole then forms a solid mass. This property is utilized in making copaiba into pills. An equal weight of official *magnesiæ carbonas* is usually employed, as, owing to its already containing hydrate, it acts more rapidly than the oxide. If time be not an object, however, the same effect may be ultimately produced by a much less quantity of magnesium oxide. The balsam from Maracaibo has been recently found to contain a new resin called metacopaivic acid, $H_2C_{22}H_{32}O_4$.

Oleum cubebæ, which is distilled from the dried unripe fruit of *Cubeba officinalis*, consists of a hydrocarbon, *cubebene* ($C_{25}H_{24}$), holding in solution a stearopten called cubeb camphor, $C_{25}H_{24}.H_2O$. The specific gravity of cubeb oil is ·92. It thickens by exposure, and rotates polarized light to the left.

Oleum coriandri, which is distilled from the fruit of *Coriandrum sativum*, is supposed to consist of a hydrated terpene, $C_{10}H_{16}.H_2O$. That this is so, is supported by the fact, that when distilled over phosphoric anhydride it yields camphene, $C_{10}H_{16}$. Its specific gravity is about ·87, and when treated with iodine a violent explosion takes place.

Oleum juniperi is distilled from the unripe fruit of *Juniperus communis*. It is described in the B.P. as being colourless or pale greenish-yellow, of a sweetish odour, and warm aromatic taste.

It consists of a terpene, $C_{10}H_{16}$, possessing the power of uniting with water, and depositing in a hydrated form $C_{10}H_{16}.H_2O$.

Oleum lavandulæ, distilled from the flowers of *Lavandula vera*, is described in the B.P. as being colourless or pale yellow, with the odour of lavender and a hot, bitter, aromatic taste.

It consists of a fluid portion containing two hydrocarbons, one of which at least is a true terpene, $C_{10}H_{16}$. The stearopten portion is similar to common camphor.

Oleum limonis is expressed or distilled from the rind of *Citrus Limonis*.

Characters.—Colour, pale yellow; odour, agreeable; taste, warm and bitter.

It is a mixture of two hydrocarbons, both $C_{10}H_{16}$, but differing in their action on polarized light. It is slightly soluble in water, and more so in alcohol, one part dissolving in seven parts of rectified spirit. By exposure it oxidizes, and deposits a substance called citroptene, to which, however, no exact formula has been affixed.

Oleum menthæ piperitæ and *oleum menthæ viridis*, obtained by distillation from the respective fresh flowering herbs, are neither truly isomeric with terpene. The former contains a liquid portion called menthene, $C_{10}H_{18}$ and a solid stearopten which is a hydrated variety of the same body, $C_{10}H_{18}.H_2O$. The latter oil would seem to answer chiefly to the hydrated menthene.

Oleum myristicæ is distilled from the kernels of the fruit of *Myristica officinalis*. It is described as colourless or straw-yellow, having the odour of nutmegs. It contains a liquid hydrocarbon, and deposits by oxidation a stearopten called myristicin.

Oleum myristicæ expressum is not a volatile oil, but a fatty body consisting of **myristin** (*glyceryl myristate*, $C_3H_5 3C_{14}H_{27}O_2$). Care must be taken to keep distinct the two ideas of *myristicin* and *myristin*.

Oleum pimentæ, distilled from the dried unripe berries of *Eugenia Pimenta*, is, according to the B.P., colourless, or slightly reddish when recent, but becoming brown by age, having the odour and taste of pimento. Sinks in water.

It is similar in composition to oil of cloves.

Oleum rosmarini, distilled from the flowering tops of *Rosmarinus officinalis*, is stated in the B.P. to be colourless, with the odour of rosemary and a warm aromatic taste. It has a specific gravity of ·90 usually, and consists of two terpenes, forming by oxidation a stearopten similar to camphor.

Oleum sabinæ, distilled from *Juniperus sabina*, consists of a terpene, $C_{10}H_{16}$, closely resembling those of *oleum terebinthinæ*.

Oleum rutæ, distilled from *Ruta graveolens*, is a pale-yellow oil, containing a terpene, $C_{10}H_{16}$, together with euodic aldehyd, $C_{11}H_{22}O$.

Gutta percha, the concrete juice of *Isonandra gutta*, and *Caoutchouc*, the well-known *indiarubber* of commerce, consist of a terpene, **caoutchin**, $C_{10}H_{16}$, and another hydrocarbon, called **isoprene**, C_5H_8, and in addition, the former contains another polymeric oil, called **heveene**. When heated, both substances melt, and then lose their elastic properties. They are soluble in turpentine, carbon disulphide, and benzol, and the latter combines easily with sulphur, forming, when the sulphur is present in small quantity, *vulcanized* rubber, and when in larger proportion, vulcanite. Gutta percha is an excellent insulator for covering electric apparatus, because, besides being a perfect non-conductor, it is not permeable by moisture.

CHAPTER XIV.

THE ALCOHOLS.

THE numerous compound basylous radicals produced by the various degrees of self-saturation of carbon atoms, and their combinations with hydrogen when so self-saturated, possess the power of forming hydrates by uniting with one or more molecules of the acidulous radical hydroxyl, in an exactly similar manner to the metals the hydrates of which we have already described. These hydrates are called **alcohols** from the fact of ordinary alcohol being the first of the series which was investigated and described. The whole of these organic hydrates are characterized by certain reactions which they exhibit in common, and more especially by possessing the power of forming neutral compounds with acids, the action being always accompanied by the elimination of water, formed by the union of the displaceable hydrogen of the acid with the hydroxyl contained in the alcohol. In formulating the alcohols, it is only necessary to remember the atomicity of the radical which gives them birth, and to add the proper number of molecules of HO; thus, the monad radical ethyl, C_2H_5, will have for its alcohol C_2H_5HO (common alcohol) which is called a **monatomic alcohol.** The dyad radical ethene, C_2H_4, will in turn form C_2H_42HO, known as a **diatomic alcohol,** or **glycol,** while the triad radical propenyl, C_3H_5, will produce C_3H_53HO, thus yielding a **triatomic alcohol** (glycerin). These classes have now to be discussed seriatim.

I. MONATOMIC ALCOHOLS OF THE SERIES $C_nH_{2n+1}HO$.

This series commences with methyl hydrate, CH_3HO, and ends with melissyl hydrate, $C_{30}H_{61}HO$, as shown by the following table :—

NAME.	FORMULA.	BOILING POINT.	MELTING POINT.	WHENCE OBTAINED.
Methyl hydrate or Methylic alcohol	$CH_3.HO$	151°F.	...	Destructive distillation of wood
Ethyl „ „ Ethylic „	$C_2H_5.HO$	173°	...	Fermentation of sugar
Propyl „ „ Propylic „	$C_3H_7.HO$	206°	...	„ grape husks
Butyl „ „ Butylic „	$C_4H_9.HO$	233°	...	„ beet root
Pentyl „ „ Amylic „	$C_5H_{11}.HO$	270°	...	„ potatoes
Hexyl „ „ Caproic „	$C_6H_{13}.HO$	309°	...	„ grape husks
Heptyl „ „ Œnanthic „	$C_7H_{15}.HO$	343°	...	Distillation of castor oil with KHO
Octyl „ „ Caprilic „	$C_8H_{17}.HO$	356°	...	Fermentation of grape husks
Nonyl „ „ Nonylic „	$C_9H_{19}.HO$	392°	...	See general processes
Decyl „ „ Rutic „	$C_{10}H_{21}.HO$	414°	...	Oil of rue
Dodecyl „ „ Lauric „	$C_{12}H_{25}.HO$	...	...	Whale oil
Hexdecyl „ „ Cetylic „	$C_{16}H_{33}.HO$	...	122°F.	Spermaceti
Ceryl „ „ Cerylic „	$C_{27}H_{55}.HO$	...	174°	Chinese wax
Melissyl „ „ Melissic „	$C_{30}H_{61}.HO$	...	185°	Beeswax

As soon as we pass the first two members, viz., methyl and ethyl, we may have several isomeric modifications of each alcohol, in addition to the true normal compound. These modifications are explained and classified by Kolbe as follows: Methyl alcohol, CH_3HO, is called a **carbinol**, and every other alcohol is simply also a more complex carbinol formed by the displacement of H in the original carbinol by some radical of the series C_nH_{2n+1}. By this view, starting with the primary carbinol, we have :—

Carbinol	$CH_3.HO$	$= CH_3HO$	primary	Methyl alcohol
Methyl carbinol	$CH_2.CH_3.HO$	$= C_2H_5HO$	,,	Ethyl ,,
Ethyl carbinol	$CH_2.C_2H_5.HO$	$= C_3H_7HO$	,,	Propyl ,,

If, however, H_2 be displaced from carbinol by two molecules of a radical, the result is a **secondary alcohol**, which differs from the primary alcohol in boiling point and in the products of its oxidation. Thus :—

Dimethyl carbinol	$CH.(CH_3)_2HO$	$= C_3H_7HO$	Propyl alcohol (secondary)
Ethyl-methyl carbinol	$CH.CH_3.C_2H_5HO$	$= C_4H_9HO$	Butyl alcohol ,,

Finally, we may proceed farther, and have a tertiary modification, in which the whole H_3 of the carbinol has been displaced by equivalent values of other radicals of the same series. For example :—

Trimethyl carbinol	$C.(CH_3)_3HO$	$= C_4H_9.HO$	Butyl alcohol (tertiary)
Dimethyl-ethyl carbinol	$C.(CH_3)_2.C_2H_5.HO$	$= C_5H_{11}HO$	Pentyl alcohol ,,

So that taking, for instance, butyl alcohol, we have three isomers, viz. :—

$C_4H_9.HO$, normal Butyl alcohol	$CH_2.C_3H_7.HO$ (or Propyl carbinol.)	boiling at 233° F.,
$C_4H_9.HO$, secondary ,, ,,	$CH.CH_3.C_2H_5.HO$ (or Methyl ethyl carbinol.)	,, ,, 207° F.,
$C_4H_9.HO$, tertiary ,, ,,	$C.CH_3.CH_3.CH_3.HO$ (or Trimethyl carbinol.)	,, ,, 179° F.,

Ordinary **primary alcohols**, when subjected to oxidation, form firstly an **aldehyd**, and secondly an **acid**, having *the same number of carbon atoms as the alcohol*, but **secondary alcohols** yield a **ketone**, instead of an aldehyd, and afterwards (by extreme oxidation only) *an* **acid** *having a less number of carbon atoms than the alcohol.* **Tertiary** alcohols yield neither aldehyd nor ketone by oxidation, but one or more acids of the acetic type.

It is only in the primary alcohols that we have much interest, and we will therefore chiefly refer to them; but before considering each individually, the following general methods of making any alcohol of the series $C_nH_{2n+1}HO$ should be understood.

1. By acting on the corresponding **paraffin** with chlorine, we obtain a corresponding haloid ether. This is then mixed with argentic acetate, forming the acetate of the required basylous radical, which, when distilled with **potassium hydrate, yields the alcohol.** Example :—

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$
$$CH_3Cl + AgC_2H_3O_2 = CH_3.C_2H_3O_2 + AgCl.$$
$$CH_3.C_2H_3O_2 + KHO = CH_3HO + KC_2H_3O_2.$$

2. From the corresponding **olefine** with sulphuric acid, and then distilling **with water** :—

$$C_2H_4 + H_2SO_4 = C_2H_5H.SO_4.$$
$$C_2H_5H.SO_4 + H_2O = C_2H_5HO + H_2SO_4.$$

3. From the corresponding **haloid ether** by simply acting with potassium hydrate, or better with argentic oxide in the presence of water, thus :—

$$2C_2H_5I + Ag_2O + H_2O = 2C_2H_5HO + 2AgI.$$

4. Any alcohol may also be prepared from that immediately below it in the series by taking advantage of the isomerism of cyanides and nitrils already referred to under cyanides. Thus, starting with methyl alcohol, we prepare methyl iodide, from this we then form methyl cyanide by the action of potassium cyanide. By now digesting methyl cyanide with sodium hydrate we obtain sodium acetate, which, by distillation with potassium formate, yields acetic aldehyd. Lastly, by acting on the aldehyd with nascent hydrogen, we obtain ethyl alcohol.

$$
\begin{array}{llcl}
CH_3HO + & HI & = & CH_3I + H_2O. \\
CH_3I + & KCN & = & CH_3.CN + KI. \\
CH_3.CN & + NaHO + 2H_2O & = & NaC_2H_3O_2 + NH_3 + H_2O. \\
NaC_2H_3O_2 + & KCHO_2 & = & C_2H_3O.H + KNaCO_3. \\
C_2H_3O.H + & H_2 & = & C_2H_5.HO.
\end{array}
$$

The various decompositions which alcohols suffer in forming haloid, simple or compound ethers, aldehyds, acids, etc., will be fully considered under their respective headings in future chapters.

METHYL HYDRATE (SYNS. *Methylic Alcohol. Carbinol. Wood Spirit. Wood Naphtha. Pyroxylic Spirit. Pyroligneous Spirit*). **Formula, CH_3HO. Molecular Weight, 32. Specific Gravity at 59° F. ·814.**

Was discovered by Taylor in 1812, and is one of the products of the destructive distillation of wood. It can also be obtained from some essential oils, and similar vegetable constituents. It may be made by direct synthesis from inorganic materials, by mixing methyl hydride (marsh gas, CH_4) with chlorine, and exposing the mixture to sunlight. This yields methyl chloride, CH_3Cl, which is converted into methyl hydrate by heating for some days to 212° F. with potassium hydrate. In the manufacture of wood spirit, the wood is enclosed in retorts, and subjected to heat. At the end of the distillation a very complex distillate is obtained, containing about one hundredth part of wood spirit. The lighter portions of the distillate are poured off, mixed with calcium oxide, and redistilled at steam heat; which process is repeated until a sufficiently pure product has been obtained.

If it be desirable to produce a still purer spirit, the last distillate is mixed with calcium chloride, when a considerable amount of heat is generated, and a combination is formed having the formula $CaCl_2.CH_3HO$, which is not decomposed at steam heat. The whole is redistilled below 212°. The impurities pass over, leaving the compound already referred to in the retort. The residual liquor is mixed with water, which causes the separation of the pure methyl hydrate, when it is once more rectified over calcium oxide.

Methyl hydrate is a colourless and very mobile liquid, burning in the air with a flame which is rather paler than that of ordinary "alcohol." It possesses a characteristic odour, has a specific gravity of ·798 at 68° F., and boils at 151° F. It may be preserved without change in contact with the air, but in the presence of an oxidizing agent, such as platinum black, it is converted into its acid (formic) $HCHO_2$; which by boiling with potassium carbonate, yields potassium formate. When treated by processes similar to those already described as applicable to ordinary "alcohol," it yields chloroform and bromoform, but not iodoform. A mixture of 90 per cent. of ordinary "spirit of wine" and 10 per cent. of wood spirit, constitutes commercial **methylated spirit,** used in the arts and in the laboratory, but which, being totally unsuited for internal administration, is not liable to duty. As, however, it is sometimes said to be substituted by the unprincipled, either in part or wholly, for "spirit of wine" in medicinal preparations, its detection becomes a matter of importance.

(*See Author's* **Analytical Chemistry,** *page* 195.)

ETHYL HYDRATE (SYNS. *Alcohol. Ethylic Alcohol. Spirit of Wine. Vinic* [*absolute*] *Alcohol*). **Formula, C_2H_5HO. Molecular Weight, 46.**

Is obtained from wine and other fermented liquors, and from these it may be separated by distillation at steam heat, and concentrated by frequent redistillation. Alcohol is always produced when sugar or any vegetable substances containing saccharine matters are subjected to the process known as fermentation. There are several varieties of fermentation, each of which takes place in a specific manner, producing a characteristic result, and is induced either by certain nitrogenous bodies, or by the presence of minute living organisms, chiefly vegetable.

The class produced by simple chemical means are sometimes called "false fermentations," while those induced by the presence of organisms receive the name of "true fermentations."

Among the former may be noted :—

The saccharine fermentation, which is the change of starch into dextrin, and of dextrin into sugar, by the action of a nitrogenous substance, called **diastase.** This change is the one which takes place during the germination of seeds when planted in the ground, and also in the artificially-produced germination of barley, known as *malting* The barley is steeped in water, and then spread on a floor, in a house specially constructed for the purpose, in which a proper temperature is maintained, coupled with the free access of air, and the exclusion of light to a considerable extent. Under these conditions the grain swells, and the action of the diastase commences; the starchy matter of the barley takes up the elements of water, and is converted into dextrin and sugar by a simple re-arrangement of its constituents, thus :—

$$\underset{\text{(Starch.)}}{3C_6H_{10}O_5} + \underset{\text{(Water.)}}{H_2O} = \underset{\text{(Dextrin.)}}{2C_6H_{10}O_5} + \underset{\text{(Glucose.)}}{C_6H_{12}O_6}.$$

When the action is judged to have proceeded sufficiently, it is stopped by transferring the malt to a kiln, in which it is subjected to heat The production of malt in this way is the first step in the commercial manufacture of alcohol The chief remaining false fermentations are :—

1. The production of volatile oil of bitter almonds by the action of a ferment called **emulsin** upon the **amygdalin** of bitter almonds, thus :—

$$\underset{\text{(Amygdalin.)}}{C_{20}H_{27}NO_{11}} + \underset{\text{(Water.)}}{2H_2O} = \underset{\text{(Oil of Bitter Almonds.)}}{C_7H_5OH} + \underset{\text{(Hydrocyanic Acid.)}}{HCN} + \underset{\text{(Glucose.)}}{2C_6H_{12}O_6}.$$

Emulsin is sometimes termed *synaptase.*

2. The production of volatile oil of mustard by the action of **myrosin** upon the **potassium myronate** of black mustard seed, thus :—

$$\underset{\text{(Potassium Myronate.)}}{K_2C_{20}H_{38}S_4N_2O_{19}} = \underset{\text{(Volatile oil of Mustard.)}}{2C_3H_5CNS} + \underset{\text{(Hydrogen-Potassium Sulphite.)}}{2(KHSO_3)} + \underset{\text{(Glucose.)}}{2C_6H_{12}O_6} + H_2O.$$

3. The change of **tannic acid** into **gallic,** by the action of a ferment which has not yet been isolated, but which exists in the galls and becomes active when they are steeped in water and exposed to warmth, thus :—

$$\underset{\text{(Tannic Acid.)}}{C_{27}H_{22}O_{17}} + 4H_2O = \underset{\text{(Gallic Acid.)}}{3H_3C_7H_3O_5} + C_6H_{12}O_6.$$

4. The action, when starchy matters are chewed in contact with the saliva of the mouth, which is due to the presence of a ferment called **ptyalin.**

5. The action which is exerted by the pancreas, and which aids in the digestion of fatty matters taken in our food, which is determined by a ferment called **pancreatin.**

6. The digestion, in the stomach, of fleshy matters, by means of a ferment called **pepsin.**

The chief of the "true fermentations," is that which is employed in the manufacture of alcohol, and consists of the conversion of sugar into alcohol, in the presence of *yeast.*

This ferment, when examined under the microscope, is found to consist of an immense mass of cells continually increasing in number. They are generally held by observers of the present day to be of vegetable origin, and to constitute the *yeast-plant*, or *Torula cerevisiæ.*

When a solution containing the special variety of sugar called *glucose* is mixed with yeast, and maintained at a temperature of 65° to 85° F., the action immediately commences, and the sugar becomes converted almost entirely into carbonic acid gas and alcohol, thus :—

$$\underset{\text{(Glucose.)}}{C_6H_{12}O_6} = \underset{\text{(Alcohol.)}}{2C_2H_5HO} + 2CO_2.$$

Besides these bodies, small quantities of other matters are produced, and M. Pasteur gives the following as the exact result of the fermentation of 105·36 grammes of pure glucose :—

Alcohol	51·11
Carbonic Anhydride	49·42
Succinic Acid	·67
Glycerin	3·16
Cellulose, and other matters of the yeast-plant	1·00
	105·36

In the ordinary commercial fermentations, when malt is used instead of sugar, the formation of alcohol is accompanied by the production of many other substances, and notably of amyl hydrate.

The remaining "true fermentations" are :

1. Acetic fermentation ; which is the change of alcohol into acetic acid, and takes place when fermenting liquors are freely exposed to the air.

2. Lactic fermentation ; which is the change of organic matters into lactic acid by the action of a ferment, and most easily originates in milk.

Alcohol is met with commercially in one or other of the following forms :—

I. **Spiritus Rectificatus.** *Rectified Spirit of Wine*, or (simply) *Rectified Spirit.*

Is prepared commercially by a process which has three distinct steps.

1. *The preparation of the mash.*—The flour of grain of various kinds, and frequently crushed potatoes, is mixed with a little malt obtained as already explained. The whole is then soaked with warm water, and beaten to a mash in a suitable apparatus. When thoroughly reduced to a pulp, it is allowed to stand for some hours, and by the action of the diastase in the malt, the saccharine fermentation sets in, and the whole becomes a translucent fluid, with a sweet taste.

2. *The fermentation of the mash.*—The liquid obtained in the last process is mixed with yeast, and allowed to ferment until the sugar has been sufficiently changed into alcohol, which is known by its decrease in specific gravity, called by distillers its *degree of attenuation.*

3. *The distillation of the fermented mash.*—The attenuated liquor is introduced into a still, where it is heated, and a very dilute alcohol is obtained, which is then concentrated by a redistillation in a special apparatus. This process is called *rectification*, and is continued until the spirit is of the desired strength.

Rectified Spirit, B.P., contains 84 per cent. of alcohol, and is colourless, transparent, very mobile and inflammable, of a peculiar pleasant odour, and a strong spirituous burning taste. Burns with a blue flame, without smoke. Specific gravity, 0·838. Remains clear when diluted with distilled water (absence of oily and resinous matters). Odour and taste purely alcoholic (freedom from aldehyd and amyl hydrate). Four fluid ounces, with thirty grain measures of the volumetric solution of argentic nitrate, exposed for twenty-four hours to bright light, and then decanted from the black powder which has formed, undergo no further change when again exposed to light with more of the test (presence of a trace only of aldehyd and amyl hydrate, the B.P. allowing an amount of these impurities equivalent to $2\frac{1}{4}$ grains of argentic nitrate per pint of spirit, as it would be impossible to obtain commercial alcohol entirely pure).

II. **Spiritus Tenuior** (SYN. *Proof Spirit*).

Is a mixture of rectified spirit and water, containing 49·25 per cent. by weight of alcohol, or 56·85 per cent. by volume, at 60° F. It is prepared by mixing five pints of rectified spirit with three pints of pure water, and its specific gravity should be ·920.

When the water and spirit are mixed, a reduction in volume of the whole takes place; so that if 100 volumes of rectified spirit be mixed with sixty volumes of water, the resulting *proof spirit* would only measure 156 volumes.

In applying to alcohol the dilution test (for oils and resinous matters), or in making proof spirit, the mixture must be allowed to stand for some time before an opinion is formed of the presence or absence of these bodies. The reason for this delay is, that distilled water almost invariably contains air, which, though soluble in water, is almost insoluble in dilute spirit. On the addition of the latter, therefore, it is expelled from solution in the form of small bubbles, which by reflecting the light in every direction, impart to the solution an opalescent appearance.

Proof spirit owes its name to the fact that it is the excise unit, according to which the duty is charged; and in former times, before the invention of hydrometers, the excise officers used to put spirit to the proof by moistening a little gunpowder with the sample, and applying a light; when, if the spirit were stronger than *proof*, the gunpowder would take fire. In calculating the strength of spirit, the legal instrument for use in this country is Sykes' hydrometer, which is floated in the spirit, and a reading being taken, together with the temperature of the spirit, a set of tables (sold with the instrument) is referred to, and the strength of the spirit, over or under proof, is ascertained. As this hydrometer becomes unavailable for mixtures containing a large percentage of sugar, endeavours are being made to encourage the discovery of a process by which it may be possible to determine the amount of alcohol in any mixture, no matter how composed, by one single operation.

Proof spirit being considered as unity, it is evident that spirit of wine, B.P., which requires to be diluted with water in the proportion to make 100 volumes up to 156, is itself 56 degrees over proof. In the same way, a spirit which requires that water should be added until 100 volumes measure 130 before it is reduced to proof strength, would be 30 degrees over proof.

III. **Absolute Alcohol** is prepared by keeping one pint of rectified spirit in contact with $1\frac{1}{2}$ ounce of dry potassium carbonate in a stoppered bottle for two days, and then distilling over 10 ounces of freshly-burned quicklime at a temperature not exceeding 200° F. The first $1\frac{1}{2}$ fluid ounce which comes over should be rejected.

Thus prepared, ethyl hydrate is a colourless, volatile, and mobile liquid,

having a specific gravity of ·795, which should show perfect freedom from water by not turning anhydrous cupric sulphate blue.

It registers (according to the Inland Revenue calculation) 74 per cent. over proof by Sykes' hydrometer.

Alcohol is a powerful preserver of animal and vegetable substances, and is therefore used as an antiseptic. It is employed in analysis as a solvent, and also as a precipitant of many substances from a watery solution. Precipitates which are slightly soluble in water are frequently washed with dilute alcohol, and it is also employed to some extent as a reducing agent. A solution of potassium chromate, for example, when heated with hydrochloric acid and a few drops of alcohol, becomes reduced to chromic chloride. When the vapour of alcohol is passed through a red-hot tube, it deposits carbon and evolves carbonic acid gas and steam, together with a complex mixture of hydrocarbons. It burns in the air, producing carbonic anhydride and water. In contact with a heated spiral of platinum wire, or a little platinum-black, the vapour of alcohol undergoes a slow and imperfect combustion, yielding very irritating vapours containing carbonic, acetic, and formic acids, together with aldehyd, acetyl, and water. Heated with soda-lime, it evolves hydrogen and forms acetates of the metals sodium and calcium.

Strong nitric acid oxidizes it rapidly with a violent evolution of gas and production of heat. Excess of alcohol, heated at a proper temperature with strong sulphuric acid, yields ethyl oxide (ether), but if the acid be in excess, and the temperature high, ethylene (olefiant gas) is produced instead.

The metals potassium and sodium decompose alcohol, evolving hydrogen, and forming potassium or sodium ethylate. This body is also formed in alcoholic solutions of potassium hydrate; but when such solutions are exposed to the air for a long time, they eventually decompose, and form a resinous matter and potassium acetate.

When alcohol is mixed with water, considerable heat is evolved, and the resulting dilute spirit has a different specific gravity from that which would be expected by calculation. Owing to the great difficulty of preserving it, pure alcohol has only a very limited number of applications.

BUTYL HYDRATE (SYNS. *Propyl Carbinol. Tetryl Hydrate*). Formula, C_4H_9HO, or $CH_2.C_3H_7.HO$.

Is of interest because frequently contained in the fusel oil which is used to prepare pharmaceutical valerianates. It can be procured from the majority of samples of the commercial fusel oil by fractional distillation, the portion coming over between 220° and 240° F. being chiefly butyl hydrate.

AMYL HYDRATE (SYNS. *Amylic Alcohol. Isopentyl Hydrate. Isobutyl Carbinol. Oil of Grain*). Formula, $C_5H_{11}HO$, or $CH.(CH_3)_2.C_2H_4.HO$.

Is produced in an impure form (*as fusel oil*) during the fermentation of potatoes, and when the spirit is distilled it passes over with the last portions of the distillate, which are milky.

It may be purified by digestion with calcium hydrate and hot water, rectifying over calcium chloride at a temperature not far from 270° F., rejecting that which comes over below 265° or above 275° F. It is contained in ordinary spirit derived from farinaceous sources (especially from raw grain and potatoes), and is dangerous to health when present to any considerable extent in spirits intended for drinking purposes, a small quantity causing giddiness, nausea, and other unpleasant symptoms. A few drops of the pure

amyl hydrate will produce all the effects of a large quantity of spirit, leaving the partaker in a most deplorable condition.

Fusel oil is a colourless liquid, with a penetrating and oppressive odour and a burning taste. When pure, its specific gravity is ·818, and its boiling point 270° F., or 5° lower than that of the normal alcohol. Sparingly soluble in water, but soluble in all proportions in alcohol, ether, and essential oils. Exposed to the air in contact with platinum-black, it is slowly oxidized, yielding isovaleric acid.

When ignited it produces a white flame. Phosphorus and sulphur are slightly soluble in amylic alcohol. By heating with potassium dichromate and sulphuric acid, valerianic aldehyd, acid and amyl valerianate are formed. When a mixture of potassium and calcium hydrate is treated with amyl hydrate, at 428° F. in closed vessels, potassium valerianate is produced and hydrogen liberated.

In ordinary amyl hydrate there are said to be two modifications, one of which does not affect polarized light, whilst the other causes right-handed rotation.

HEXDECYL HYDRATE (Syns. *Cetyl Alcohol. Ethal*). **Formula, $C_{16}H_{33}.HO$.**

Prepared from spermaceti (*cetaceum*, B P.), a crystalline fatty body found in the head of the sperm whale. In cetaceum the radical $C_{16}H_{33}$ takes the place which in most fats is occupied by glyceryl, C_3H_5, and spermaceti is therefore nearly pure cetyl palmitate, $C_{16}H_{33},C_{16}H_{31}O_2$, sometimes termed cetine. The spermaceti is saponified with caustic potash, and the cetyl alcohol formed is dissolved out by alcohol and afterwards purified by crystallizations from ether. Hexdecyl hydrate is a tasteless, odourless, white crystalline mass. It melts at about 122° F. It dissolves freely in alcohol, but is insoluble in water. It distils at a high temperature and without decomposition. Heated with potash and lime, it is converted into palmitic acid, with evolution of hydrogen.

CERYL HYDRATE (Syns. *Cerotic Alcohol. Cerotine*). **Formula, $C_{27}H_{55}.HO$.**

This alcohol is obtained from Chinese wax, which is chiefly composed of ceryl cerotate. It is prepared by saponification much in the same manner as cetyl alcohol. It is a wax-like substance, melting at 206·6° F. It distils at a high temperature with partial decomposition. When heated with a mixture of potash and lime, it gives off hydrogen, and is converted into cerotic acid.

MYRICYL HYDRATE (Syns. *Melyl or Melissyl Alcohol*).
Formula, $C_{30}H_{61}.HO$.

This is the highest member of the $C_nH_{2n+1}HO$ series at present known. It contains over 82 per cent. of carbon, whereas methyl alcohol, the lowest of the series, contains only 40 per cent.

It is obtained by saponification from myricine (the portion of beeswax insoluble in boiling alcohol, and which consists of myricyl palmitate), the process being the same as that employed for cetyl and ceryl alcohol. Thus prepared, myricyl alcohol is a crystalline substance having a silky lustre. It melts at about 185° F. When heated it sublimes with partial decomposition. Heated with potash lime it is converted into potassium melissate with evolution of hydrogen.

II. MONATOMIC ALCOHOLS OF THE SERIES $C_nH_{2n-1}HO$.

Only one alcohol of this series has been obtained, namely, allyl alcohol. The substance known as vinyl alcohol was long placed in this series; but recent researches have shown it to consist of crotonic aldehyd.

ALLYL ALCOHOL. Formula, $C_3H_5'.HO$.

Prepared indirectly from glycerin by submitting it to the action of diphosphorous tetriodide, when allyl iodide is obtained:—

$$2C_3H_5'''(HO)_3 + P_2I_4 = 2C_3H_5'.I + 2H_3PO_3 + I_2.$$

The allyl iodide is then decomposed by silver oxalate, when allyl oxalate is formed:—

$$2C_3H_5'.I + Ag_2C_2O_4 = (C_3H_5)_2'C_2O_4 + 2AgI.$$

The allyl oxalate is next submitted to the action of ammonia, when oxamide and allyl hydrate are produced:—

$$(C_3H_5)_2C_2O_4 + 2NH_3 = C_2O_2N_2H_4 + 2C_3H_5'HO.$$

Allyl alcohol is a colourless liquid having a burning taste and a mustard-like spirituous smell. It burns with a bright flame and is miscible in all proportions with water, alcohol, and ether. Boiling point, 217·5° F. Allyl alcohol is a primary alcohol, and in all ordinary reactions behaves like ethyl alcohol. By the action of platinum black or a mixture of sulphuric acid and bichromate of potash, allyl alcohol is transformed first into acroleïne and then into acrylic acid. Strong H_2SO_4 converts it into allyl sulphuric acid, $C_3H_5'HSO_4$.

III. DIATOMIC ALCOHOLS, OR GLYCOLS, $(C_nH_{2n})''2HO$.

The glycols are derived from the saturated hydrocarbons by the substitution of 2HO' for 2H. Like the monatomic alcohols, they furnish ethers, aldehyds, and acids; but while the former can only yield one each of these derivatives, the glycols, being diatomic, generally yield two of each and pass through two successive steps of etherification, dehydrogenation, and oxidation.

The glycols are formed by the following general processes:—An olefine is combined with bromine, and the dibromide formed is treated with silver acetate, and thus converted into a glycol diacetate. The diacetate is now acted on by potassium hydrate, when it yields potassium acetate and the required glycol.

The glycols are colourless, inodorous, viscid liquids having a sweetish taste; freely soluble in water and alcohol. When subjected to the action of oxidizing agents they give up two or four atoms of hydrogen in exchange for oxygen and yield two distinct acids.

METHYLENE HYDRATE (Syn. *Methylene Alcohol*). **Formula, CH_22HO.**

Is not at present known, though ethylene hydrate, the next member of the series, is easily obtained.

ETHYLENE HYDRATE (Syns. *Glycol. Ethyl Glycol. Ethylene Alcohol*). **Formula, C_2H_42HO.**

Is procured by treating ethylene acetate with potassium or barium hydrate.

$$C_2H_42C_2H_3O_2 + 2KHO = C_2H_42HO + 2KC_2H_3O_2.$$

The ethylene acetate is the result of acting upon ethylene bromide, produced by direct combination of ethylene (olefiant gas) and bromine with potassium or argentic acetate. It is of interest as yielding oxalic acid by oxidation. Glycol, as it is usually termed, is a syrupy, colourless liquid, soluble in water and alcohol, but only dissolving in a relatively large amount of ether. It boils at 387° F., and has a specific gravity of 1·125. It dissolves many bodies which are soluble in alcohol. When diluted with water, and the solution brought in contact with platinum-black, glycollic acid, a body intermediate between glycol and oxalic acid, is formed, having the formula $C_2H_2O.2HO$. Heated with potassium hydrate to 480° F., hydrogen is eliminated and potassium oxalate produced.

$$C_2H_4 2HO + 2KHO = K_2C_2O_4 + 4H_2.$$

PROPYLENE HYDRATE (SYNS. *Hydrate of Tritylene. Propylene Alcohol. Trityl Glycol*). **Formula, $C_3H_6.2HO$.**

Is not of pharmaceutical interest except as the source of derivation of lactic acid. Prepared like ethylene hydrate.

TETRYLENE, or BUTYLENE HYDRATE (SYNS. *Tetrylene* or *Butylene Alcohol. Butyl* or *Tetryl Glycol*). **Formula, $C_4H_8.2HO$.**

Owes its interest to the fact that it yields succinic acid by oxidation. It may be produced by acting upon *tetrylene acetate*, with potassium hydrate, as in the preparation of glycol.

IV. TRIATOMIC ALCOHOLS OF THE SERIES $C_nH_{2n-1}.3HO$.

These hydrates may be regarded as derived from a triple molecule of water, H_6O_3, by substitution of a trivalent alcohol radical for three atoms of hydrogen. The triatomic alcohols are able to exchange part or the whole of their hydroxyl for a halogen element or acid radical, thus glycerin forms three **hydrochloric ethers** :—

1st. $C_3H_5'''Cl(HO)_2$, 2nd. $C_3H_5'''Cl_2(HO)$, and 3rd. $C_3H_5'''Cl_3$,

which are known as **chlorhydrins**, and are obtained by the direct action of hydrochloric acid upon glycerin. There are only two triatomic alcohols known, namely, propenyl hydrate or glycerin, and pentenyl or amyl glycerin.

GLYCERYL HYDRATE (SYNS. *Glycerin. Propenyl Alcohol. Glyceric Alcohol*). **Formula, $C_3H_5.3HO$.**

This important body is a bye-product in the preparation of the fatty acids for the purpose of making soap and candles, and also in the pharmaceutical preparation of *lead plaster*. It exists free in palm oil and some other varieties of vegetable oils, whence it can be dissolved out by agitation with hot water, and (as has been already shown under **Alcoholic Fermentation**) is formed in the production of wine and beer.

Formerly *glycerin* was entirely obtained by the saponification of olive oil with plumbic oxide, but its great liability to contain lead when thus prepared has caused the almost total discontinuance of this process.

If it be desirable to procure a small quantity for experimental or other purposes, plumbic oxide and olive oil are heated together until the B.P. lead plaster is formed, and the aqueous liquor is purified from lead by means of a

stream of sulphuretted hydrogen gas; the liquid after filtration is then very gently evaporated to a syrup.

The process which is most generally employed at the present time, is one depending upon the dissociation of the acids and the glycerin of fats by the action of steam at about 580° F. The distillate which results consists of an aqueous solution of glycerin with the fatty acids floating upon its surface. The lower layer is drawn off by a tap near the bottom of the condenser and receiver combined, and the greater part of the water is removed by evaporation. When thus prepared, and its specific gravity rendered as high as possible by evaporation, glycerin is a clear, colourless fluid, oily to the touch, without odour, and of a sweet taste.

It cannot be crystallized, and is soluble in water in all proportions, neutral to test-paper, decomposes almost entirely on being heated, and when absolutely free from water exhibits a specific gravity of 1·26 at 60° F. although the commercial article rarely exceeds 1·25. Glycerin dissolves as readily in alcohol and chloroform as in water, but ether entirely fails to take it up. Iodine is soluble to a large extent in glycerin, forming an orange solution, but no chemical action takes place. Glycerin forms salts with hydrates somewhat resembling saccharates, but less readily decomposed. For example, calcium, barium, and strontium saccharates are decomposed by carbonic anhydride, but the glycerin compounds of these metals are not. Potassium and sodium hydrates, and all salts having a great affinity for water, and consequently deliquescent, dissolve in glycerin. But this is not the only class of salts which it dissolves, for it takes up sodium sulphate, which has so little affinity for water as to be positively efflorescent; also zinc and potassium sulphates, potassium and sodium chlorides, sodium carbonate, and others. The solubility of plumbic oxide in glycerin explains the fact that, when obtained by the action of plumbic oxide on olive oil, it always contains lead in solution. Insolubility in water, as a rule, also implies insolubility in glycerin; but many exceptions exist. If mixed with potassium hydrate, no precipitate is formed when an excess of the mixture is added to a solution of cupric sulphate. Some alkaloids and their salts are taken up entirely by glycerin; others dissolve if heated, but separate out on cooling. If then the mass be rubbed while cooling, an emulsion is formed. All carbonaceous acids are taken up by this remarkable solvent.

The solutions of carbolic, gallic, and tannic acids in glycerin are official. The B.P. also contains a solution of borax, and a mucilaginous starch mixture in this liquid.

Glycerin may be recognised by the following characteristics :—

1. Its specific gravity.
2. Its powerlessness to rotate polarized light.
3. It should be easily and entirely soluble in chloroform, otherwise it contains glucose.
4. Sodium hydrate, when heated with it, produces no brown colour (absence of glucose).
5. By heating with strong sulphuric acid, extremely acrid and irritating vapours are evolved, which are called *acrolein*, C_3H_4O. These vapours are especially irritating to the eyes, and cause a copious flow of tears. Zinc chloride, phosphoric anhydride, or acid potassium sulphate, may be substituted for the sulphuric acid. If an aqueous solution of glycerin be employed, it must be rendered as strong as possible by evaporation, to ensure the success of this test.

The action of nitric acid upon glycerin produces, according to dilution and temperature, either nitro-glycerin or a mixture of glyceric and oxalic acids. It precipitates gold from auric chloride.

The salts of glyceryl formed from glycerin are generally called by special names derived from that of the acid which may be contained in them, by substituting *in* or *ine* for *ic*.

Thus, glyceryl mon-acetate, $C_3H_5.C_2H_3O_2.2HO$, is termed mon-acetin, glyceryl tri-palmitate, tri-palmitin. In cases in which all of the hydroxyl of the glyceryl hydrate is not displaced, the whole of the name of the acid except the last syllable is prefixed to the word *hydrin*: thus, mon-acetin would be mon-acet-hydrin. Usually, however, it is the hydrochloric derivatives to which this class of appellations is applied, because of the inconvenience of a word bearing so near a resemblance to chlorine as *chlorin*.

NITRO-GLYCERIN. Formula, $C_3H_5(NO_2)_3O_3$.

A terribly explosive agent, obtained from glycerin by the action of a mixture of strong nitric and sulphuric acids in substituting nitryl for hydrogen. It is a heavy, oily liquid, and explodes violently by percussion. *Dynamite*, *litho-fracteur*, and other blasting compounds, all depend for their activity on the presence of nitro-glycerin, usually finely divided by being mixed with sand, etc.

V. HEXATOMIC ALCOHOLS.

In this class of substances are included three of the natural sugars, mannite, dulcite, and sorbite, and the compounds known as saccharoses. The glucoses and the amyloses are also included as derivatives, they however demand a special chapter to themselves.

MANNITYL HYDRATE (SYNS. *Mannite. Mannitic Alcohol*).
Formula, $C_6H_8.6HO$.

This body exists to the extent of 60 to 80 per cent. in *manna*, B.P., from which it may be extracted by alcohol. The natural sources are officially stated to be the *Fraxinus Ornus* and *F. rotundifolia*, and from these it is obtained by making incisions in the stems of trees cultivated for the purpose, chiefly in Sicily. The following official plants also contain mannite to a greater or less extent, *Aconitum Napellus*, *Punica Granatum*, and *Canella alba*. It may be obtained artificially by subjecting glucose ($C_6H_{12}O_6$) to the action of nascent hydrogen (evolved from sodium amalgam and water), when the decomposition shown below occurs:—

$$C_6H_{12}O_6 + Na_2 + 2H_2O = C_6H_8.6HO + 2NaHO.$$

Manna is met with in commerce in stalactiform pieces from one to six inches in length, and one or two inches in width, uneven, porous, and friable, curved on one side, of a yellowish white colour, with a faintly nauseous odour and a sweetish taste. It consists principally of mannite, together with common sugar and extractive matter. The mannite, which forms from 60 to 80 per cent. of the manna, may be extracted by means of boiling rectified spirit, from which it will afterwards separate on cooling in colourless, shining crystals. It requires five parts of cold water for its solution, and this does not undergo vinous fermentation in contact with yeast.

Several recrystallizations from alcohol are required to produce it in a pure state. Unlike most sugars, mannite may be very readily crystallized from its aqueous solution, and without uniting with any water. The alcohol best adapted for dissolving mannite is that of 60 per cent., in which it dissolves to the extent of 1·25 per cent. in the cold, but much more extensively when

heated. It does not dissolve in ether, but water takes up about 15·6 per cent. at the normal temperature. It is optically inactive, but its adulterations and substitutions rotate a polarized beam of light. Mannite melts at 330° F. By oxidation it yields mannitic acid, $C_6H_{12}O_7$, and mannitose, $C_6H_{12}O_6$. With nitric acid it yields saccharic acid, and ultimately oxalic acid. Heated with organic acids it forms compound ethers which are termed mannitanides. It does not form a precipitate when heated with cupric tartrate and potassium hydrate in excess, nor does it turn brown when boiled with the latter alone. Mannite is formed when sugar undergoes the mucous fermentation (which takes place by the action of a nitrogenous ferment in the presence of air), and may be obtained from the evaporated solution by extraction with hot alcohol. Ergot of rye (*ergota*, B.P.) sometimes contains mannite, as also some *algæ* and *fungi*.

VI. ALCOHOLS OF THE AROMATIC SERIES.—PHENOLS.

The displacement of more or less hydrogen from benzene by hydroxyl yields a series of alcohols called **phenols**. They differ from ordinary alcohols by having a somewhat acidulous nature and forming comparatively very stable compounds with metals.

They may be prepared by heating the aromatic oxy-acids with calcium oxide, when carbonic anhydride is given off and the phenol distils over. Thus salicylic acid so treated yields phenyl hydrate (carbolic acid).

$$C_7H_6O_3 = C_6H_5.HO + CO_2$$

Of all organic series the aromatic is the most interesting; but we are limited by our scheme to the consideration of those members employed in medicine or pharmacy.

PHENYL HYDRATE (Syns. *Phenol. Carbolic Acid. Phenic Acid. Coal Tar Creasote*). **Formula, C_6H_5HO.**

Is a constituent of *castoreum*, B.P., and may be obtained by heating salicylic acid; but in practice it is procured from coal tar by distilling until a solid substance (anthracene) begins to come over. The product is then placed in another retort, and the distillate passing over between 360° F. and 390° F. is mixed with a solution of potassium hydrate containing some undissolved potassium hydrate in powder, when the oily liquid immediately becomes solid. It is then dissolved in hot water, and after some time the lower liquid is drawn off by any convenient means. Hydrochloric acid is next added until the liquid becomes neutral; and the supernatant fluid, having been drawn off, is agitated with water, and, after digestion with calcium chloride for the purpose of absorbing the water, is subjected to several distillations. On cooling the final distillate to −18° F., pure phenyl hydrate crystallizes out. Phenyl hydrate fuses at 93° to 95° F., forming a colourless oily fluid. The crystals of the pure acid absorb moisture readily from the air, a very slight quantity causing their deliquescence from colourless needles to a liquid similar to that formed by the application of heat. Calcium chloride removes the moisture, consequently giving rise to an instantaneous resolidification. Though termed an acid, it does not affect litmus like other members of the acid class. It is a powerful antiseptic. When pure, it is met with in colourless acicular crystals, which at a temperature of 95° become an oily liquid having a strong odour and taste, resembling those of creasote, which it also resembles in many of its characters and properties. Its specific gravity is

1·065; boiling point, 370° F. It is only slightly soluble in water, but is freely soluble in alcohol, ether, and glycerin; coagulates albumen and does not affect the plane of polarization of a ray of polarized light. A slip of deal dipped into it and afterwards into hydrochloric acid, and then allowed to dry in the air, acquires a greenish-blue colour.

Concentrated sulphuric acid converts it into phenyl hydrogen-sulphate (sulpho-carbolic acid, $C_6H_6HSO_4$). By passing ammonia gas into a solution of phenyl hydrate, and heating the result in a closed tube, a small quantity of ***aniline*** (phenylamine, $C_6H_5.H_2N$) is formed:—

$$C_6H_5HO + NH_3 = C_6H_5.H_2N + H_2O$$

A solution of potassium hydrate does not dissolve it in proportion to its strength, and unlike all true acids (except hydrocyanic), it does not decompose carbonates. None of the combinations are of pharmaceutical interest, except those produced by the action of ammonia gas, sulphuric acid, and nitric acid. If it be acted upon by ammonium hydrate and chlorinated lime, it gives rise to a blue liquid, which wood, or true creasote does not produce. From the latter it also differs by its capability of ready solidification; true creasote not becoming solid at −49° F. Phenyl hydrate does not become solid after being melted, whereas if creasote be heated to 212° F. and maintained at that temperature for some hours, a solid residue remains.

The following are some other points of distinction:—

Phenyl Hydrate.	**Creasote.**
Inactive towards polarized light.	Dextro-rotatory.
Commercial glycerin dissolves it.	Does not dissolve it.
It precipitates nitro-cellulose from an ethereal solution in a gelatinous form.	Does not cause any effect when added to the same solution (known as *collodium*, B.P.).
Alcohol and ferric chloride yield a brown colour.	Alcohol and ferric chloride yield a green coloration.
Ferric chloride and a little ammonium hydrate produce a violet colour.	Ferric chloride and ammonium hydrate give rise to a green coloration fading to brown.

Creasote consists chiefly of creasol ($C_8H_{10}O_2$), a volatile liquid of a pleasant odour, which differs from phenyl hydrate in reducing the metal from argentic nitrate, and forming an almost insoluble crystallizable salt with ammonium hydrate. Creasol must not be confounded with cresyl hydrate (C_7H_7HO), a volatile liquid which is isomeric with the next substance we are about to consider. The radical contained in creasol being monad renders it almost impossible to regard that body as an "alcohol," because all alcohols possessing a monad radical contain a single atom of oxygen only.

Phenyl hydrate being a dangerous poison can only be employed medicinally in very small doses. Should it accidentally happen that an excessive quantity has been taken, fixed oils will serve to mitigate the effect, olive, almond, and castor oils being the most useful. The following are the qualities of true **wood creasote**:—

A liquid, colourless or with a yellowish tinge, and a strong empyreumatic odour. It is sparingly dissolved by water, but freely by alcohol, ether, and glacial acetic acid. Specific gravity, 1·071. It coagulates albumen. A slip of deal dipped into it, and afterwards into hydrochloric acid, acquires on exposure for a short time to the air a greenish-blue colour. Dropped on white filtering paper, and exposed to a heat of 212°, it leaves no translucent

stain. It turns the plane of polarization of a ray of polarized light to the right. It is not solidified by the cold produced by a mixture of hydrochloric acid and sulphate of soda.

BENZYL HYDRATE (SYNS. *Benzylic Alcohol. Benzoic Alcohol. Toluylic Alcohol*). **Formula, C_7H_7HO.**

Is of inconsiderable importance to pharmacists, but gives birth to two highly interesting products by oxidation. These are **benzoic aldehyd** (essential oil of bitter almonds) and **benzoic acid,** the basis of benzoates. The hydrate itself is made by decomposing benzoic aldehyd by means of a solution of potassium hydrate in alcohol, when the following rather remarkable reaction occurs :—

$$2C_7H_5O.H + KHO = C_7H_7.HO + KC_7H_5O_2.$$

When balsam of Peru (*balsamum Peruvianum,* B.P.) is warmed with potassium hydrate in aqueous solution, an oil rises to the surface. If this be separated, and distilled in an atmosphere of carbonic anhydride at the lowest possible temperature, the distillate contains benzyl hydrate.

CINNYL HYDRATE (SYNS. *Cinnamic Alcohol. Storax Alcohol. Styrone Peruvin*). **Formula, C_9H_9HO.**

Is prepared by distilling balsam of Peru with water, boiling the residue with sodium carbonate solution (forming styracin) and redistilling the insoluble portion with potassium hydrate. If salt be added to the liquid passing over, a solid body gradually forms on the surface, which is cinnyl hydrate. When pure, this body is composed of smooth needle-like crystals, possessing an odour of hyacinths. The crystals, when first formed, are extremely small; but when the solution is allowed to stand they gradually increase in size.

CAMPHYL HYDRATE, or CAMPHOL (SYNS. *Borneol. Borneo Camphor. Camphyl Alcohol*). **Formula, $C_{10}H_{17}HO$.**

This body is a "concrete volatile oil" obtained from the *Dryobalanops aromatica* of Borneo. It is one of the several substances passing under the denomination of camphors, but is not that in general use. Like other alcohols it yields ethers (salts) by the action of acids, water being eliminated. Camphol may be obtained from common (or China) camphor by heating it with an alcoholic solution of potassium hydrate in a sealed tube. The reaction is at some times less complex than at others, the following equation representing the most simple :—

$$2C_{10}H_{16}O + 4KHO = 2C_{10}H_{18}O + 2K_2O + O_2.$$

Camphol melts at 388° F., and can be sublimed without decomposition at about 420° F. It is capable of conversion into ordinary camphor by the action of nitric acid, and is distinguished from the latter by not becoming liquid when treated with hydrochloric acid.

CHAPTER XV.

CARBO-HYDRATES.

THESE bodies are of ternary composition, containing carbon, hydrogen, and oxygen. They form a group by themselves, being easily converted into each other by the addition or subtraction of the elements of water. Properly they are derivatives of, and should be classified with, the alcohols of hexad radicals; but for convenience we have placed them separately. Their connection, however, with hexad alcohols may thus be theorized :—

1. The hexad alcohol, by subtraction of hydrogen, may be supposed to yield an aldehyd :—

$$\underset{\text{(Mannite.)}}{C_6H_86HO} + O = \underset{\text{(Glucose.)}}{C_6H_{12}O_6} + H_2O.$$

2. The aldehyd, by subtraction of water from two or more molecules, may yield a polyglucosic alcohol :—

$$\underset{\text{(Glucose.)}}{2C_6H_{12}O_6 - H_2O} = \underset{\text{(Saccharose.)}}{C_{12}H_{22}O_{11}}.$$

3. A polyglucosic alcohol, by further loss of water, may yield an oxygen-ether.

$$\underset{\text{(Saccharose.)}}{C_{12}H_{22}O_{11}} - H_2O = \underset{\text{(Starch.)}}{2C_6H_{10}O_5}.$$

It is a fact worth noting, that in all these bodies the carbon exists combined with just sufficient hydrogen and oxygen to always form a definite number of molecules of water.

They are divided into three isomeric classes, corresponding with the above-mentioned reactions, as follows.*

---

* Those marked + are dextro-rotary to polarized light, while those marked − are lævo-rotary.

AMYLOSES, ($C_6H_{10}O_5$).	SACCHAROSES, ($C_{12}H_{22}O_{11}$).	GLUCOSES, ($C_6H_{12}O_6$).
Cellulose.	+ Cane sugar.	+ Grape sugar.
Starch.	+ Milk sugar.	− Fruit sugar.
+ Dextrin.	+ Maltose.	Mannitose.
− Inulin.	+ Melitose.	+ Galactose.
Glycogen.	+ Melezitose.	Inosite.
Gums.	+ Trebalose.	Sorbin.
	+ Mycose.	Eucalin.
	+ Parasaccharose.	

I. AMYLOSES,

OR CARBO-HYDRATES OF THE GENERAL FORMULA $C_6H_{10}O_5$.

CELLULOSE (SYNS. *Cellulin. Lignin*). **Formula, $C_6H_{10}O_5$.**

Is the material of which the walls of the cells of plants are composed. The best-known forms of cellulose are cotton and linen, and its reactions may be learned by acting on either of these substances. It is official as *gossypium*, B.P., which is the carded hairs of the testa of the cotton plant. Cellulose is insoluble in water and also in dilute acids and alkalies, its best solvent being a deep-blue liquid obtained by dissolving cupric oxycarbonate in ammonium hydrate. When thus in solution it is re-precipitable by a slight excess of acid, in the form of white flakes which are not affected by tincture of iodine.

The woody fibre of plants is an impure form of cellulose, containing usually more hydrogen, together with a little nitrogen. When cellulose is stirred into *cold* strong sulphuric acid, it is converted into a soluble gum similar to *dextrin*, and by diluting and boiling this solution *glucose* is produced.

Vegetable Parchment (SYN. *Papyrin*), used in dialysis, has a composition analogous to cellulose, and is prepared by passing unsized paper through tolerably strong sulphuric acid, and then washing, first with pure water and afterwards with water containing a little ammonium hydrate.

The **estimation of woody fibre** is a matter which is important in the analysis of vegetable matters. It is conducted by boiling a weighed portion of the article, first in dilute sulphuric acid and then, after filtration and thorough washing, once more boiling the insoluble portion in dilute solution of potassium hydrate. The whole, having been filtered, is finally washed with boiling water, dried at 212°, and weighed.

Nitro-cellulose (SYNS. *Pyroxylin. Gun Cotton*).

When cellulose is treated with nitric acid, a substitution of nitryl takes place for one or more atoms of hydrogen, and one of the three following varieties of nitro-cellulose is produced:—

Mononitro-cellulose, $C_6H_9(NO_2)O_5$.
Dinitro-cellulose, or *Pyroxylin*, B.P., $C_6H_8(NO_2)_2O_5$.
Trinitro-cellulose, or *Gun Cotton*, $C_6H_7(NO_2)_3O_5$.

In practice the nitric acid is mixed with sulphuric acid, because it is found to cause the former acid to act more quickly; but it does not affect the real reaction, of which the following may be taken as a type, choosing dinitro-cellulose as the one most interesting to pharmacists and medical men:—

$$C_6H_{10}O_5 + 2HNO_3 = C_6H_8(NO_2)_2O_5 + 2H_2O.$$

The following table shows the characteristics of each of the three varieties:—

Mononitro-cellulose. *Not soluble* in a mixture of alcohol and ether; *soluble* in acetic acid. (Not very inflammable.)

Dinitro-cellulose. *Soluble* in the former; *insoluble* in the latter. (Tolerably inflammable.)

Trinitro-cellulose. *Soluble* in both. (Very inflammable.)

The following are the instructions as to making and testing *pyroxylin*, B.P. (which is dinitro-cellulose).

Take of

Cotton	1 ounce.
Sulphuric Acid } Nitric Acid }	5 ounces.

Mix the acids in a porcelain mortar, immerse the cotton in the mixture, and stir it for three minutes with a glass rod, until it is thoroughly wetted by the acids. Transfer the cotton to a vessel containing water, stir it well with a glass rod, decant the liquid, pour more water upon the mass, agitate again, and repeat the affusion, agitation, and decantation, until the washing ceases to give a precipitate with chloride of barium. Drain the product on filtering paper, and dry in a water bath.

Tests.—Readily soluble in a mixture of ether and rectified spirit; leaves no residue when exploded by heat.

The vapours set free when it explodes (which it does at 300° F.), liberate iodine from potassium iodide, thus rendering paper soaked in that substance and starch paste, blue; they also show an acid reaction with litmus.

When 1 ounce of pyroxylin is dissolved in a mixture of 36 fluid ounces of ether and 12 fluid ounces of alcohol, **collodium**, B.P., is produced.

It is a colourless highly inflammable liquid with ethereal odour, which dries rapidly upon exposure to the air, and leaves a thin transparent film, insoluble in water or rectified spirit.

STARCH (SYN. *Amylum*). **Formula, $C_6H_{10}O_5$.**

Is a white granular body stored up in the stems, roots, and seeds of plants, and is the most abundant proximate principle found in the vegetable kingdom. It is separated from the plant tissues by steeping them for some time in water rendered just alkaline with sodium hydrate, and then rubbing the softened mass on a sieve under a slow stream of water. The fibre and glutinous matters remain on the sieve, while the starch passes through with the water, from which it is recovered by settlement, and finally drying at an exceedingly low heat. The ordinary *patent starch* used in laundries is usually prepared from rice by the above process, and then coloured slightly blue with indigo, and dried in lumps. Pure starch is a white powder with a peculiarly slippery feel between the fingers, and insoluble in cold water, alcohol, ether, and other common solvents. When examined under a microscope with a ¼-inch object glass, it is seen to be made up of rounded transparent bodies, each formed by an albuminous coat filled with gelatinous starch which is called *amidin*. Many of these *granules* possess a spot, or *hilum*, round which are collected a number of parallel annular depressions known as *rings*. The base of all starch is amidin, but the starch of each plant possesses some special characteristic, either in size, shape, hilum, or rings, which enables us to identify it with tolerable certainty. When starch is moistened with cold water and a quantity of boiling water stirred in, the granules swell and burst, and a mucilaginous liquid is obtained, but no true solution takes place. This preparation is called *mucilago amyli* in the B.P.

A similar effect is produced by heated glycerin, the result being called *glycerinum amyli* (SYN. *Plasma*).

By boiling with water and a few drops of a dilute acid, an alteration in the starch slowly takes place, and it is converted first into a mixture of **dextrin** and **glucose**:—

$$3C_6H_{10}O_5 + H_2O = 2C_6H_{10}O_5 + C_6H_{12}O_6.$$

On prolonging the boiling, more water is taken up, and the whole is converted into **glucose**:—

$$2C_6H_{10}O_5 + 2H_2O = 2C_6H_{12}O_6.$$

By the action of nitric acid, starch is converted into oxalic acid.

The best test for starch is to make a decoction of the article under examination, and *when cold* add a drop of iodine solution, which will produce a

fine blue colour, which is amidin iodide. (*See* **Iodine.**) Under the microscope the presence of starch granules is fully confirmed by adding a drop of tincture of iodine, which colours them deep purple.

Amylum, B.P., is described as the starch procured from the seeds of common wheat, *Triticum vulgare*. It should be met with in white columnar masses. When rubbed in a Wedgwood mortar with a little cold distilled water, it is neither acid nor alkaline to test-paper, and the filtered liquid does not become blue on the addition of solution of iodine Mixed with boiling water and cooled, it gives a deep blue colour with iodine.

INULIN. Formula, $C_6H_{10}O_5$.

Is an isomeric variety of starch met with in the root of *Inula Helenium* and many other plants. It is, like starch, insoluble in cold water, but freely soluble in boiling water, from which it deposits on cooling. By boiling with a dilute acid it is entirely converted into levulose. It is insoluble in alcohol and is turned brown by iodine, but does not precipitate with plumbic acetate or infusion of galls.

GLYCOGEN. Formula, $C_6H_{10}O_5$.

Is a white tasteless body resembling starch, found in the liver of animals, and especially a constituent of the tissues of the fœtal embryo. It is soluble in water and insoluble in alcohol.

DEXTRIN (SYN. *British Gum*). **Formula, $C_6H_{10}O_5$.**

This substance may be produced by three methods. That most commonly adopted consists simply in "baking" starch at a temperature approaching 350° F. Thus procured it is a yellowish powder, which dissolves in cold water, forming a somewhat gum-like solution, and when mixed with various colours is employed in the arts for calico-printing and other similar purposes.

Upon boiling starch with water and a few drops of sulphuric acid, the mixture becomes perfectly limpid after a few minutes, owing to the conversion of the starch into dextrin. If the sulphuric acid be neutralized by calcium carbonate and the precipitated calcium sulphate separated by filtration, and the filtrate be evaporated to dryness by a heat of 212° F., a residue of dextrin mixed with some glucose remains. The glucose may be removed by digesting with dilute alcohol, in which dextrin is insoluble. Too long boiling with acid will entirely convert the starch into glucose; but if conversion into dextrin be effected by malt or diastase, no amount of boiling will decompose the dextrin thus formed. When seeds undergo germination, a peculiar nitrogenous ferment becomes active. It is termed **diastase**, and appears to be vegetable albumen in a state of metamorphosis. When a little malt (in which a considerable amount of diastase exists) is mixed with more than a hundred times its weight of gelatinous starch, and heated to 160° F., in the course of ten minutes or less, the mixture will become as mobile as water.

The fact of starch invariably forming glucose as well as dextrin when treated with acids (which are not themselves affected, acting only by introducing the elements of water into the molecules of the starch) has led to the deduction that the molecular formula of starch must be $C_{18}H_{30}O_{15}$, and the reaction when it is boiled with acid requires then to be represented as follows :—

$$C_{18}H_{30}O_{15} + H_2O = C_6H_{12}O_6 + 2C_6H_{10}O_5.$$

True dextrin must be carefully distinguished in the mind from the ordinary gummy and mucilaginous matters of plants. The **gums**, properly so called,

are exudations from various parts of plants, chiefly from the stems. The leaf buds of the *poplar*, however, yield gum, as also the roots of the *Malvaceæ* and *Orchidaceæ*. The mucilage of fruits does not contain gum, but **pectin**. (*See* **Glucosides.**)

[redacted]

Arabin, $CaC_{12}H_{20}O_{11}$, is the soluble portion of *acaciæ gummi*, B.P., which exudes from the stems of one or more undetermined species of *Acacia*. It is found in commerce as spheroidal tears usually from half an inch to an inch in length, nearly colourless, and opaque from numerous minute cracks, or in fragments with shining surfaces; brittle; bland and mucilaginous in taste; insoluble in alcohol, but soluble in water. The aqueous solution forms with subacetate of lead an opaque white jelly (plumbic gummate). If an aqueous solution of iodine be added to the powder, or to a solution formed with boiling water and cooled, there is no appearance of a violet or blue colour (absence of starch).

When arabin is boiled with dilute acid it is converted into glucose, which might be expected, seeing that gummic acid, $H_2C_{12}H_{20}O_{11}$, is really isomeric with cane sugar, $C_{12}H_{22}O_{11}$.

By the action of strong nitric acid, arabin forms **mucic acid**, and may be further distinguished from dextrin by not being precipitated by cupric sulphate. Any solution suspected to contain arabin may be tested by adding a few drops of ferric sulphate solution, when, if gum be present, the whole will become a jelly.

Cerasin and **bassorin** are two other forms of gum: the former is produced by cherry trees, and the latter constitutes the chief portion of *tragacantha*, B.P., an exudation from the stem of *Astragalus verus*. It is insoluble in cold water, but readily absorbs that fluid, so that it swells into a jelly. Besides bassorin, tragacanth contains a little arabin, starch, and fibre, and corresponds to the following official description and tests.

Characters. White or yellowish, in broad shell-like slightly curved plates, tough and elastic, but rendered more pulverizable by a heat of 120° F.; very sparingly soluble in cold water, but swelling into a gelatinous mass, which is tinged violet by tincture of iodine (presence of a trace of starch only). After maceration in cold water the fluid portion is not precipitated by the addition of rectified spirit (absence of adulteration by soluble gums).

A formula of $C_{12}H_{20}O_{10}$ has been assigned to bassorin, but it is only doubtful.

II. SACCHARHOSES,

OR SUGARS OF THE GENERAL FORMULA, $C_{12}H_{22}O_{11}$.

The principal members of this family are:—

Saccharose, or **Sucrose**. Which is by far the most important.

Para Saccharose. Produced by the spontaneous rearrangement of the molecules of saccharose under the influence of diammonium phosphate.

Melitose. Contained in the Tasmanian manna, yielded by various species of *Eucalyptus*.

Melezitose. Is yielded by the manna of a species of *Larix* (larch), growing in Switzerland.

Trehalose. "Trehala manna," the product of a tree of Asiatic growth, is the source of this substance.

R

Mycose. Is produced from *ergota*, B.P., by the treatment of a solution of ergot in water with plumbic acetate, the decomposition of the lead salt remaining in the clear liquid obtained by filtration, with hydrogen sulphide, and evaporation, after again filtering, to the crystallizing point.

These two substances both contain two molecules of water of crystallization.

Lactose. Contains a molecule of water of crystallization. It is next to sucrose in importance amongst the members of the class under consideration, and besides that body, is the only one worthy of detailed notice.

Maltose. Is the sugar existing in malt, and is very similar to glucose, but more optically active, rotating a ray of polarized light three times as much to the right. It appears by the latest researches however to be an isomer of lactose, and is obtained when diastase acts on starch.

SUCROSE. Cane Sugar (SYNS. *Saccharose. Beetroot Sugar. Saccharum Purificatum, B.P.*). **Formula,** $C_{12}H_{22}O_{11}$.

Procured from the sugar-cane (*Saccharum officinarum*) cultivated in both the Indies. It is also produced from the sugar maple (*Acer saccharinum*) of North America; in Germany, and specially in France, from the beetroot, in which it is contained to the extent of 8 per cent. or thereabouts. The edible nuts consumed in most parts of the world usually contain several per cent. of sucrose; and it is an abundant constituent of the juice of most grasses, of the sap of large trees, of the "nectar" of the majority of *cacti*, and of carrots, parsnips, turnips, and most roots.

The sugar-cane, in which no other sugar than sucrose exists, is the source from which the greater bulk of the sugar consumed in the world is obtained. It contains 18 to 20 per cent. of crystallizable sucrose, and the preparation is conducted as follows:—

The canes are crushed between rollers, and the juice allowed to flow into a large cistern placed beneath. Thence it passes into large pans, in which it is heated approximately to 212° F., and then a mixture of calcium hydrate and water is added, by which mechanical impurities, vegetable wax and albumen, and calcium phosphate, are thrown down, and the solution is neutralized to prevent its conversion (as much as possible) into inverted sugar. The clear liquid produced on subsidence is run off into another vessel, evaporated to the crystallizing point, and then stirred frequently, so as to produce the granular form of "raw," "moist," or "muscovado" sugar. Were it not stirred, a dark coloured variety of "sugar-candy" would result. In order to remove the mother liquor (called "molasses") from the product, it is put into barrels, perforated at one end, and standing with that end downwards.

At the present time it is customary to evaporate the juice in "vacuum pans" (large closed vessels from which air pumps serve to remove the air, together with the aqueous vapour evolved during the progress of the evaporation). When these are employed, the evaporation is much more rapid, and, as it takes place below 150° F. instead of above 230° F., much less waste is caused from the production of uncrystallizable sugar.

Recently, machinery has been introduced which will remove the juice much more completely than the rollers commonly employed. A solid piston moves horizontally in a cylinder which it fits closely. This cylinder is closed at one end, and the cane having been introduced by a somewhat similar contrivance to that used in a chaff-cutting machine, the piston, at each stroke, cuts a slice off the end of the cane, and crushes it against the portion of the cylinder towards which it is moving, provision for the exit of juice being made by suitable apertures. The sap is much more thoroughly extracted by this

contrivance, by which the canes are compressed transversely, than by the rollers, which crush them longitudinally.

Beetroot and maple sugar, when "raw," possess a peculiar taste, which nothing but habit renders agreeable for daily use. The former, however, when refined, is very nearly undistinguishable from cane sugar. The refining of sugar is practised chiefly in this country. It consists in removing the mechanical matters from a solution of "raw" sugar by adding albumen, either in the form of white of egg or *serum* of blood. The liquid is then filtered, first through canvas, to remove the coagulum, and afterwards through animal charcoal to remove the colour; it is next evaporated to the crystallizing point at 160° F. in vacuum pans, and poured into earthen moulds, where it solidifies into masses of minute crystals, as seen in ordinary "loaf sugar." Lastly, a saturated solution of pure sugar is passed through, by which the last traces of colour are removed, and the "loaf" is then dried in a stove. This is the official *saccharum purificatum.*

If a saturated, or nearly saturated, solution of cane-sugar be slowly cooled, without agitation, "sugar-candy" is formed. If sugar be liquefied without water being present, it produces a slightly yellow, transparent, amorphous mass, being in fact the substance known as "barley sugar." The crystals of "sugar-candy" are doubly oblique prisms.

Sucrose dissolves in cold water to the extent of three parts in one; in hot water it is soluble to the extent of five parts or even more in one part. Ether does not dissolve it at all, alcohol not to any notable extent, but in proof spirit it is soluble to some extent. When rubbed, or broken, in the dark, it emits a flash of violet light, exhibiting the phenomenon of "phosphorescence." It melts at 360° F., becoming transformed into a mixture of levulosan and dextrose, $C_{12}H_{22}O_{11} = C_6H_{10}O_5 + C_6H_{12}O_6$. As the heat increases water is given off and the dextrose is converted into glucosan. At about 410° F. it gives off more water, forming the *caramel*, or "burnt sugar," at one time official under the name of *saccharum ustum*, but now only employed as a colouring agent in culinary operations. Finally, it gives off inflammable gases, chiefly carbonous oxide and marsh gas, and becomes entirely decomposed. Argentic, mercuric, auric, and some other salts are decomposed when boiled with sucrose, the metals being precipitated. Yeast, in the presence of warmth and moisture, causes dextrose and levulose to be formed, which afterwards yield alcohol. Strong hydrochloric and dilute sulphuric acids transform sucrose into inverted sugar rapidly. Sucrose is readily oxidizable, exploding when mixed with potassium chlorate by percussion, and catching fire when sulphuric acid is added to the mixture. Rubbed in a mortar with plumbic dioxide it also undergoes inflammation. Treated with warm nitric acid it forms saccharic acid ($C_6H_{10}O_8$); and on boiling that product is converted into oxalic acid ($H_2C_2O_4$).

Potassium and sodium sucrates are produced by mixing the respective hydrates (in solution) with syrup. The former has the constitution, $C_{12}H_{21}KO_{11}$, the second has a similar composition. They are both gelatinous and not very soluble in water.

Sucrose is recognized by the following characteristic reactions:—

1. It gives no brown colour when warmed with dilute potassium hydrate.
2. The addition of sulphuric acid produces a black colour in a cold and dilute solution of sucrose.
3. It does not form a precipitate when boiled with "Fehling's solution" (cupric tartrate dissolved in potassium hydrate).
4. A solution of sugar rotates a ray of polarized light 73° 8′ to the right.

If inverted by treatment with dilute acid, it gives no reaction with sulphuric

acid, but produces a brown colour with potassium hydrate in excess, and a red precipitate of cuprous oxide with Fehling's solution. The *inverted sugar* thus produced rotates the polarized ray to the left 50° at 57·2° F.

Sucrose is estimated by dissolving a known weight (say 50 grains) in 10,000 grain measures of water, containing 20 drops of sulphuric acid. This liquid is boiled for six hours with addition of water to make up loss by evaporation. It is then exactly neutralized by sodium carbonate, and a known quantity (say 1000 grains = 5 grains sugar) is treated as directed under **Dextrose.**

When flour is mixed with yeast, as in bread-making, many substances are produced, amongst which the principal are sucrose and dextrin, which afterwards yield alcohol, carbonic anhydride, and succinic acid. The process of rendering bread light depends upon the evolution of the carbonic anhydride, which, by insinuating itself within the mechanical interstices of the dough, pushes the particles asunder. Thus, when the bread is introduced into the system, it presents a much larger surface to the action of the gastric juice than it would if it had not been *raised.* Ordinarily, therefore, digestibility is conjoined with lightness; and this has led to the idea that the two are inseparable in this article of diet. The so-called "aërated bread," made by mixing flour with carbonic acid solution under pressure, in special machinery contrived for the purpose, is the offspring of this fancy; and there is not the slightest reason to doubt that it is a wholesome and nutritious substance. That it is capable and worthy, however, of altogether supplanting fermented bread we cannot allow. During the course of fermentation the many substances formed render the mixture of such a complex nature that it is doubtful whether any artificial mixture could profitably be made to possess all its properties. Hence we are of opinion that neither aërated bread nor any substance made without fermentation will ever supplant fermented bread, which is at once the most wholesome, digestible, palatable, and nutritious of all edible compounds.

LACTOSE (SYNS. **Milk Sugar.** *Lactin. Saccharum Lactis, B.P.*).
Formula, $C_{12}H_{22}O_{11}.H_2O$.

Is produced by evaporating milk to the crystallizing point, after the removal of the cream by standing, and the casein by coagulation. The product, which is not perfectly white, may be decolorized by animal charcoal, after it has been redissolved in pure water. The solution, on careful re-evaporation, yields a white solid, to which the B.P. assigns the following properties:—

Usually in cylindrical masses, two inches in diameter, with a cord or stick in the axis, or in fragments of cakes; greyish-white, crystalline on the surface, and in its texture, translucent, hard, scentless, faintly sweet, gritty when chewed.

It is very slightly soluble in alcohol, and is quite insoluble in ether. Medicinally it is perfectly inactive, hence largely used in Continental pharmacy as a means of exhibiting active remedies in the form of powder. With alkaline bodies it forms salts, which are very readily decomposable. It only dissolves in cold water to the extent of 17 to 20 per cent., but is taken up by boiling water to the amount of 35 per cent. It reduces cuprous oxide from "Fehling's solution." Lactose was formerly classed as an unfermentable sugar. It has, however, been found that it will ferment after some weeks when left in contact with yeast and water at 80 to 90° F. If calcium carbonate and decaying cheese, or gluten, be mixed with warm water and lactose, calcium lactate and alcohol will be formed in the course of a few weeks, the

amount of the latter increasing as the strength of the lactose solution decreases, and depending also on the amount of calcium carbonate present.

Lactose, when oxidized with nitric acid, yields a considerable amount of mucic acid ($C_6H_{10}O_8$), whilst sugars generally give an isomer—saccharic acid. In consequence of this fact, and because gum yields mucic acid when similarly treated, it is believed that lactose forms a sort of connecting link between sugars and gums. When lactose is boiled with a dilute acid, it is converted into *galactose*, a sugar isomeric with glucose. Oxalic acid results from the sufficient oxidation by nitric acid of this as of all other sugars. Sulphuric acid and manganic dioxide produce, from lactose, abundance of formic acid. Lactose reduces silver from ammonio-argentic nitrate, in the presence of potassium hydrate, very readily. Sucrose takes a longer time and acts less perfectly. A mixture containing lactose is used for silvering specula for telescopes and other similar purposes. Lactose is estimated by precisely the same process as **Dextrose** (*which see*).

III. GLUCOSES,

OR SUGARS OF THE GENERAL FORMULA $C_6H_{12}O_6$.

The number of these bodies at present known does not exceed ten. The principal are :—

Dextrose. The most important sugar of this division.

Levulose. The result of the action of acids on the starch called *inulin.* It is also formed, together with dextrose, when sucrose is inverted.

Mannitose. Produced by the oxidation of manna.

Galactose. Produced when dilute acids act on lactose. It yields much mucic acid by oxidation, the others giving saccharic acid.

Sorbin. May be procured from mountain-ash berries, in which it exists together with malic acid.

Eucalyn. Which is the so-called "sugar" of *Australian manna.* This sugar (and also sorbin) is not readily fermentable.

Inosite. Is a species of glucose existing in the heart and other portions of the internal animal organism. It does not ferment with yeast ; but when mixed with cheese or decaying flesh, it undergoes the *lactic* fermentation. Evaporated first with nitric acid, and afterwards with ammonium hydrate and calcium chloride, it develops a rose colour.

None of the above are so definitely crystallizable as sucrose. They also produce a dark-coloured solution when boiled with dilute potassium hydrate ; give cuprous oxide, when treated with Fehling's solution ; and, when in solution in cold water, are not charred by sulphuric acid.

DEXTROSE (SYNS. **Glucose.** *Dextro-glucose. Grape Sugar*).
Formula, $C_6H_{12}O_6.H_2O$.

Is the principal form in which sugar exists in ripe fruits, and of it the crystalline grains found in dried fruits consist. It is contained abundantly in the urine of diabetic patients. If consolidated honey be washed with alcohol, the fluid portion, dissolving, leaves almost pure glucose in a granular condition. The ripe fruit of the "dog-rose" (*Rosæ caninæ fructus*, B.P.), contains dextrose and levulose, to the extent of 30 per cent. of its weight.

Five principal methods of procuring it chemically are known :—

1. By acting upon starch with diastase (a peculiar ferment found in barley which has been allowed to germinate—in other words, in malt). Treated in this manner it becomes hydrated, thus :—

$$3C_6H_{10}O_5 + H_2O = C_6H_{12}O_6 + 2C_6H_{10}O_5.$$

2. By treating starch with sulphuric acid.

Mucilage of starch is made by pouring boiling water upon the powder, and this is boiled with about 1 per cent. of sulphuric acid for five or six hours, the water lost by evaporation being supplied, from time to time, from a vessel of boiling water kept in readiness for that purpose. Afterwards calcium carbonate, in the form of chalk or whiting, is added to the liquid, until effervescence ceases. The solution is then filtered, and the filtrate, upon evaporation, leaves glucose; and if the syrupy mass be allowed to stand for three or four days, the amorphous glucose, at first separated, will be transformed into a mass of crystalline grains.

3. By making a mixture of pure dry cellulose (in such a form as "cotton-wool" or linen rags) with twice its weight of strong sulphuric acid, digesting in the cold for five or six hours, then pouring into a considerable quantity of water, filtering, boiling for a few minutes, and treating the liquid, as in the last case, with calcium carbonate. By this means more than an equal weight of sugar may be obtained from linen. It has been proposed to treat sawdust (which has been deprived of its resinous constituents) in a similar manner, but omitting to boil the filtered liquor before neutralization, in order to obtain a substance which, when mixed with a nitrogenous body, would be available as bread.

4. By boiling cane sugar with dilute acid. Thus, sucrose will yield dextrose together with its isomer, levulose, in equal proportions, the mixture being known as inverted sugar:—

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

Yeast, the ferment of fruits (denominated pectase), and spontaneous decomposition, will also cause sucrose to undergo the same metamorphosis. When the mixture of levulose and dextrose (called "inverted sugar"), obtained as detailed, is mixed with ten times its weight of *milk of lime*, containing 6 per cent. of calcium hydrate, the dextrose only remains in solution, and if the mass be pressed it is expelled. On removing the calcium from the solution, by means of carbonic anhydride, and evaporating the filtrate from the calcium carbonate thrown down, pure dextrose results.

5. Treating any natural glucoside with dilute acid causes the production of dextrose (and levulose).

Dextrose (Glucose) exhibits the following characteristic tests:—

1. Its cold watery solution is not changed by strong sulphuric acid, which distinguishes it from sucrose.

2. Heated with *liquor potassæ*, it blackens, while cane sugar does not change.

3. It precipitates cuprous oxide from Fehling's solution in a few seconds, becoming oxidized in so doing. Sucrose does not, except after long boiling.

A hundred parts require 140 of water for solution, the same quantity of sucrose requiring only 30. Glucose is also less sweet than the latter.

The crystals are distinguished from those of cane sugar by being cubical in shape, instead of prismatic, and by never presenting large plane surfaces (such as are seen in *sugar-candy*). When free from moisture, it does not lose weight when heated to 266° F.; at a temperature of 340° F., however, water is given off, and a compound called glucosan, having the same composition as dextrin, is produced; lastly, heated more strongly, it becomes *caramel*, and finally burns away. Dextrose rotates the polarized ray to the right 56°.

When subjected to prolonged ebullition with dilute acids, it is transformed into *ulmin* and some other similar bodies. Calcium, barium, and plumbic oxides are capable of union with dextrose. The two former compounds pro-

duce a salt containing three molecules of the oxide to two of glucose and two of water, thus $(CaO)_3 (C_6H_{12}O_6)_2.2H_2O$. A compound of dextrose and sodium chloride possesses the constitution, $2C_6H_{12}O_6 NaCl.H_2O$.

In consequence of sucrose having to be transformed into glucose, before the fermentative process can be set up, the latter ferments much more quickly. Heated with nitric acid, glucose forms first saccharic and afterwards oxalic acid.

There are two principal processes for the estimation of dextrose (glucose), the one gravimetric, the other volumetric. Both of these depend upon the almost instantaneous reduction of cuprous oxide from cupric tartrate in the presence of an alkaline hydrate.

(*For volumetric process, see Author's* **Analytical Chemistry**, *pages* 159, 160.)

The gravimetric estimation is performed by adding excess of Fehling's solution to 5 grains of sugar dissolved in 1000 grains of water, and boiling. The mixture is then filtered, and the precipitate of cuprous oxide on the filter dried and ignited in a tared porcelain crucible. A few drops of nitric acid are added to the residue, the liquid is evaporated to dryness very carefully with a lid on the crucible; lastly, the whole is heated to full redness for ten minutes, transferred to a desiccator, and weighed when cool. 220·5 parts of cupric oxide, the resulting product, correspond to 95 parts of cane sugar, or 100 parts of glucose. In applying this test to the estimation of lactose, it will be found that 147·76 parts of cupric oxide correspond to 100 of milk sugar.

Fehling's solution of cupric tartrate in potassium hydrate is made by dissolving 350 grains of pure crystallized cupric sulphate, reduced to powder, and pressed between bibulous paper till absolutely free from extraneous moisture, in a little distilled water, and adding 1730 grains of sodium potassium tartrate (Rochelle salts), then introducing 600 grains of pure potassium hydrate, dissolved in the smallest possible quantity of water, until the deep blue precipitate of cupric tartrate is entirely dissolved, using more of a ten per cent. solution of potassium hydrate if necessary. The liquid must then be made up to 10,000 grain-measures, and immediately introduced into a well-stoppered bottle, as the carbonic anhydride of the air causes rapid deterioration. Previously to every determination in which this solution is employed, it is necessary to boil a few drops with a quantity of pure water, and if any red precipitate is formed, the solution must be rendered incapable of producing such (when boiled with pure water) by the addition of solid potassium hydrate free from carbonate.

LEVULOSE (SYN. *Levo-glucose*). **Formula,** $C_6H_{12}O_6$.

This substance is formed artificially by boiling inulin with dilute sulphuric acid, and also, together with dextrose, when cane sugar is boiled with the same acid, and naturally in many fruits by the action of an acid or a ferment contained in the juice. It may be separated from dextrose by taking advantage of its property of forming a solid compound with milk of lime containing 6 per cent. of calcium hydrate, as mentioned under *dextrose*. The maple, rose, lime, and other trees, sometimes bear upon the leaves, and other parts, a thick excretion, which occasionally becomes sufficiently solid to lose its adhesiveness, and so falls to the ground. This saccharine substance consists of dextrose and sucrose as well as levulose, and is popularly denominated *honey dew*. Treacle and molasses (the former resulting from the purification of moist sugar, the latter from the preparation of that moist sugar from the sugar cane) contain a proportion of levulose, and also dextrose, sucrose, and colouring matter. Honey, another substance in which it exists, is sometimes

used in making confections; sucrose, however, being more frequently employed.

Levulose is met with in a colourless uncrystallizable syrup which rotates a polarized ray 106° to the left at 57·2° F. It is more soluble in alcohol than dextrose, and as sweet as sucrose. It is similar in chemical reactions to dextrose.

FRUIT SUGAR (SYNS. *Inverted Sugar. Honey Sugar*). **Formula, $C_6H_{12}O_6$.**

Is the mixture of equal parts of dextrose and levulose found in honey and many fruits, and also formed when cane sugar is boiled with dilute sulphuric acid, or warmed with strong hydrochloric acid. Owing to the excess of the lævo-rotary power of levulose over the dextro-rotary power of dextrose, inverted sugar turns the polarized ray to the left 50° at 57·2° F.

It is similar in reactions to glucose.

CHAPTER XVI.

ORGANIC ACIDS.

An acid is the result of the oxidation of an alcohol. All normal alcohols are characterized by their susceptibility to oxidation, the result of which is the production of one or more substances possessing acid properties, and forming in their turn a complete and characteristic series of salts, in consequence of the displacement of a portion of their hydrogen by the various metals and basylous radicals. The oxidation of an alcohol takes place by two distinct steps, the first of which consists in the removal of two atoms of hydrogen, and results in the formation of a body called an *aldehyd;* while in the second step the aldehyd takes to itself an additional atom of oxygen, and forms the *acid.* By distilling ordinary alcohol with any oxidizing agent, such as a mixture of manganic dioxide and sulphuric acid (*see* **Oxygen**), we obtain its aldehyd as the result of the following reaction :—

$$\underset{\text{Alcohol.}}{2C_2H_5HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Aldehyd.}}{2C_2H_4O} + \underset{\text{Water.}}{2H_2O}.$$

The aldehyd produced is extremely unstable; and by simply exposing it to the air, oxygen is at once absorbed, and acetic acid is produced ; thus,—

$$\underset{\text{Aldehyd.}}{2C_2H_4O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic Acid.}}{2C_2H_4O_2}.$$

The aldehyd is usually named after the acid, and not the alcohol ; thus, the one above referred to would be called *acetic aldehyd.* Aldehyds may be reconverted into the corresponding alcohols by the action of alkaline hydrates, a salt of the corresponding acid being simultaneously produced. Thus, benzoic aldehyd (oil of bitter almonds) yields benzyl hydrate and potassium benzoate when treated with potassium hydrate :—

$$2C_7H_6O + KHO = C_7H_7HO + KC_7H_5O_2.$$

Nascent hydrogen also reconverts aldehyds into alcohols ; example,—

$$C_2H_4O + H_2 = C_2H_5HO.$$

Aldehyds are characterized by all forming insoluble compounds with potassium hydrogen-sulphite, and this principle is taken advantage of in separating and obtaining them in a pure state.

Unfortunately the names of the acids produced by oxidation from alcohol are merely arbitrary; most of them having been discovered and named *before* the alcohol from which they are derived. This circumstance causes considerable confusion in the mind of a young student, as he has to learn that common alcohol yields acetic acid, while amyl alcohol yields valerianic acid.

In theory, the oxidation is supposed to take place by the substituti-

for H_2 in the basylous radical of the alcohol (*vide* page 210). The new radical formed is called the oxygenated or acid radical. Thus :—

The basylous radical (*ethyl*), C_2H_5 corresponds to the oxygenated radical (*acetyl*), C_2H_3O.

	of the basylous radical		corresponds to the		of the oxygenated radical	
The hydride		(*ethane*), $C_2H_5.H$		hydride		(*aldehyd*), $C_2H_3O.H$.
The hydrate		(*alcohol*), $C_2H_5.HO$		hydrate		(*acetic acid*), $C_2H_3O.HO$.
The oxide		(*ether*), $(C_2H_5)_2O$		oxide		(*anhydrous acetic acid*) $(C_2H_3O)_2O$.
The haloid ether		(*ethyl chloride*) $C_2H_5.Cl$		chloranhydride		(*acetyl chloride*) $C_2H_3O.Cl$.

These oxygenated radicals are usually named by adding *yl* to the first two syllables of the name of the acid; thus, acetic aldehyd would be named **acetyl hydride**, and its rational formula from this point of view would be $C_2H_3O.H$; while acetic acid would in turn become **acetyl hydrate**, $C_2H_3O.HO$.

As, however, the main object of the pharmacist is to obtain an acquaintance with the various acids themselves and the salts they produce by displacement of one or more atoms of their hydrogen, we adhere to the older idea, and leave the student who is desirous of learning the more advanced views on this subject to refer to any special work, such as Frankland's "Organic Chemistry." We prefer, therefore, to write a rational formula for an "organic" acid in the same way as we have done with the acids already studied, viz., by placing the displaceable hydrogen first, and viewing the rest of the acid as an acidulous radical which is to be found unchanged in all the salts produced by the acid in question.

The hydrate of a monad compound radical (usually called a **monatomic alcohol**) is only capable of forming one acid by oxidation; but such acid-forming power becomes much more extended when we arrive at the hydrates of dyads, such as ethylene, and triads, such as glyceryl. The **diatomic alcohols** (hydrates of dyads) can form two acids, according to the number of atoms of typical hydrogen affected by the oxidation. In this way ethylene hydrate (**glycol**) can produce either **glycollic** or **oxalic acids**, as follows :—

$$C_2H_4 2HO + O_2 = \underset{\text{Glycollic Acid.}}{H_2C_2H_2O_3} + H_2O.$$

$$C_2H_4 2HO + 2O_2 = \underset{\text{Oxalic Acid.}}{H_2C_2O_4} + 2H_2O.$$

The **triatomic alcohols**, like glyceryl, can form three acids in this manner, and so on through all the hydrates of polyatomic radicals, the number of possible acids increasing with the number of atoms of typical hydrogen.

I. ACIDS OF THE FATTY SERIES, $C_nH_{2n}O_2$.

These acids are derived from the alcohols of the series, $C_nH_{2n+1}.HO$. Those which can be distilled unaltered in the air are said to be volatile acids, and those which decompose when heated are called non-volatile.

They are acted upon by phosphorous oxychloride, forming acid chlorides or chlor-anhydrides; thus, acetic acid and phosphorous oxychloride yield acetyl chloride :—

$$3HC_2H_3O_2 + POCl_3 = 3C_2H_3O.Cl + H_3PO_4.$$

The acid chlorides so produced, when distilled with a metallic salt of the corresponding acid, yield the oxide of the acid radical (anhydride). Thus, acetyl chloride, distilled with sodium acetate, yields anhydrous acetic acid :—

$$C_2H_3O.Cl + NaC_2H_3O_2 = (C_2H_3O)_2O + NaCl.$$

The acid chlorides are oily liquids, fuming in the air, and breaking up into the fatty acid and hydrochloric acid on touching water.

Fatty acids heated with alcohols in sealed tubes, yield compound ethers, and conversely, the ethers produced may themselves be "saponified," or reduced to the alcohol and acid by heating with a little water in a sealed tube to over 480 F. The acids may be formed, as already shown, by oxidizing the corresponding alcohol into aldehyd, and then exposing the latter to the air, but besides this, an acid can also be formed from the cyanide of the alcohol radical next lower in the series by heating with potassium hydrate.

Thus, *methyl* cyanide may be made to yield potassium acetate:—

$$CH_3.CN + KHO + H_2O = K.C_2H_3O_2 + NH_3.$$

FORMIC ACID. Formula, $HCHO_2$, Molecular Weight, 46.

Is the result of the oxidation of methyl hydrate. It exists in the acid secretion which is furnished by the red ant (*Formica rufa*), and hence acquires its name. It is also contained in the glands of *Urtica urens* (the small nettle), and in a few mineral waters, notably those of Prinzhofen. The destructive distillation of asafœtida, the action of alkalies upon chloral, chloroform, etc, and the spontaneous decomposition of hydrocyanic acid in contact with the air, are also sources of its derivation. It is commercially prepared on the large scale by distilling oxalic acid with its own weight of commercial glycerin, when a violent disengagement of carbonic anhydride takes place, and a fluid distils over containing 56 per cent. of formic acid. It may be rendered absolutely pure by treatment with plumbic carbonate, when plumbic formate is produced, and remains in solution, but may be crystallized out by evaporation. The dried crystals of plumbic formate are then exposed to the action of sulphuretted hydrogen. The liberated acid is distilled off from the plumbic sulphide also formed, and is obtained free from sulphuretted hydrogen by passing through it a current of dried carbonic anhydride. The anhydrous acid is solid between 30° and 34 F, though at the ordinary temperature it is a syrupy, colourless liquid. By the displacement of its hydrogen by metals, and basylous radicals, it yields a class of salts termed *formates*.

Formic acid causes a precipitate of metallic mercury, when it is boiled with mercuric or mercurous nitrate It is distinguished from other acids derived from carbon (except carbonic and oxalic), by not undergoing charring, when mixed with sulphuric acid and heated. It readily reduces argentic nitrate, when mixed with a little solution of sodium hydrate, and heat applied, metallic silver separating. *It does not* reduce platinic and auric chlorides when boiled with them, *unless sodium or potassium hydrate be added.*

This is owing to the volatility of the acid. It is a fact well worthy of notice, that oxalates may be formed from formates, by heating with an excess of an alkaline hydrate.

For example, the action of potassium hydrate on potassium formate produces potassium oxalate, the hydrate remaining unaltered, and hydrogen being evolved, thus:—

$$KHO + 2KCHO_2 = K_2C_2O_4 + H_2 + KHO.$$

(*For detection of Formic Acid and Formates, see Author's* **Analytical Chemistry**, *page* 74.)

HYDROGEN ACETATE (SYNS. **Acetic Acid.** *Acetyl Hydrate. Pyroligneous Acid*). **Formula, $HC_2H_3O_2$. Molecular Weight, 60.**

This very common and useful acid results from (1) the oxidation of alcohol, (2) the dry distillation of wood, and (3) the action of the mineral acids upon

acetates. It is contained in the juices of some plants, and in certain animal secretions.

The dilute form, well known as "vinegar," is *acetum*, B.P., which is obtained from wine in France, and from fermented malt liquor in England.

Wine which has gone sour is mixed with wine lees, and after standing in contact for a time, the mass is placed in cloth sacks, and pressed until no more liquid flows. The solution thus obtained is fermented in casks having a small opening at the top, and heated to about 80° F. This occupies, in summer, not more than a fortnight; in winter, rarely less than a month. The vinegar is transferred to casks containing a little birchwood, and after standing for a fortnight, to clarify, is ready for use.

A quick process for its manufacture is adopted in Germany, and only requires a day, or a day and a half, for its accomplishment. A thin stream of the alcoholic liquid falls into a wooden tube containing shavings of beech wood, whilst air is allowed to pass upwards through holes in the side of the tube. The rapid oxidation of the alcohol, in consequence of the large amount of its surface exposed to atmospheric action, raises the temperature to more than 100° F., but this may be lowered, if it be thought desirable, by allowing a more rapid stream to flow. After passing three or four times down this tube, the liquor is completely acetified.

Malt vinegar is made by exposing a fermenting solution of malt and unmalted grain to the air for five or six months. A better process is by placing casks, containing the fermented solution of malt (*see* **Alcohol**), in dark rooms, covering the tops with coarse cloths, and exposing them to a temperature approaching to 90° F. The duration of this process is not fixed, varying from several weeks to three or four months. When acetification has ceased to occur, the product is filtered several times through the residue obtained after the preparation of British wines, which is known as *rape*.

Though it has for a long time been proved that the idea of preserving vinegar by the addition of sulphuric acid, is erroneous, most manufacturers continue to add at least the amount allowed by Act of Parliament: viz., 1 part per thousand of vinegar.

Vinegar, B.P., is an acid liquid of a brown colour and peculiar odour. Specific gravity, 1·017 to 1·019. Vinegar is essentially a dilute solution of acetic acid, containing some colouring and extractive matters derived from the malt, and a trace of flavouring compound ethers formed during fermentation.

Owing to the inferior volatility of acetic acid to water, a simple distillation does not, as in the case of spirit, secure a stronger distillate, but a weaker. Hence the *distilled vinegar*, commonly supposed to be stronger than the ordinary coloured form, contains a less percentage of acetic acid.

The pharmaceutical forms of acetic acid are derived from wood. This source is cheaper than the ones which we have detailed, but the resulting acid is much more difficult to obtain in a pure state. Wood is placed in a large iron retort, and heated until no more vapours are evolved. The distillate is separated into two portions, a *watery* and a *tarry* product. The watery part is redistilled at a heat below boiling water. The spirituous constituent then passes over, and the residue is crude acetic acid, usually called pyroligneous acid, on account of its empyreumatic odour. It must be mixed with calcium carbonate and sodium sulphate, until the liquid is neutral and no more precipitate is formed by the addition of either. The clear solution, after filtration, is evaporated to crystallization; and the crystals of sodium acetate which separate, having been heated until most of the tarry matter is destroyed or driven off, are further purified by crystallization, and then decomposed by an equivalent quantity of sulphuric acid mixed with half its weight of water. In consequence of the inability of strong acetic acid to dissolve sodium

sulphate, the greater proportion of this crystallizes out, and may be removed. The acid is purified from the slight amount of sulphate remaining in solution by redistillation.

A cheaper process consists in the saturation of the crude wood products with calcium oxide, filtration of the liquid, evaporation to half its bulk, and rendering it slightly acid by the addition of about one-fiftieth of its weight of hydrochloric acid. This causes the tarry matters to float upon the surface, whence they are eliminated by skimming. The clear solution is evaporated to complete dryness, mixed with about one tenth of its weight of water, and four fifths of its weight of B.P. hydrochloric acid, and then distilled.

A distillate, having the specific gravity of 1·200, is obtained. By heating the product with about three per cent. of potassium dichromate, and distilling, any excess of hydrochloric acid is destroyed, and a peculiar odour which the acid formerly possessed disappears.

The B.P. acetic acid contains 33 per cent. of real acetic acid, $HC_2H_3O_2$, corresponding to 28 per cent of anhydrous acetic acid, $C_4H_6O_3$ or $(C_2H_3O)_2O$.

It is a colourless liquid, having a strong acid reaction and a pungent odour. Specific gravity, 1·044.

When the acid above described is diluted with water to eight times its bulk, the B.P. *acidum aceticum dilutum* results, having a specific gravity of 1·006.

Another form of the acid is official, viz., *acidum aceticum glaciale*, B.P. This is nearly pure acetic acid, containing only about $1\frac{1}{4}$ per cent. of water.

Potassium acetate combines with acetic acid to form potassium diacetate, $KC_2H_3O_2.HC_2H_3O_2$. When therefore a tolerably strong (acetic) acid is mixed with potassium acetate it retains part of the acid when subjected to distillation. If this mixture be distilled until the distillate has a specific gravity of 1·065, and a dry receiver be used to collect the product which afterwards comes over, the glacial acid may be procured. The mode of preparation in more general use is by the distillation of a neutral acetate with sodium hydrogen sulphate, or with strong sulphuric acid. Glacial acid ought to be pure acetic acid, but in commerce it contains about 98·8 per cent. of $HC_2H_3O_2$, corresponding to 84 per cent. of anhydrous acid, $C_4H_6O_3$.

It crystallizes when cooled to 34°, and remains crystalline until the temperature rises to above 48°. Specific gravity, 1·065 to 1·066, and this is increased by adding ten per cent. of water. At the mean temperature of the air it is a colourless liquid, with a pungent acetous odour. The form of acetic acid which passed under the name of "spirits of copper" and "spirits of verdigris" is still made by the dry distillation of cupric acetate, freed from moisture by a heat of 220° to 250° F.

Pure acetic acid crystallizes at a temperature somewhat less than 60° F., except when secluded from atmospheric action, in which case an analogous phenomenon to "supersaturation" occurs, and the liquid retains its normal form, even when reduced to 53·5° F.; a slight shake, however, of the opened vessel causing rapid solidification and a decided rise in temperature. It boils when raised to 243° F. The liquid is not inflammable, though its vapour is. When strong sulphuric acid is heated with it, charring ensues. The acid containing 21 per cent. of water is the heaviest form, having a specific gravity of 1·073. This is a curious circumstance, contrary to the general properties of liquids, and likely to give considerable annoyance to any person who, being unaware of the fact, attempts to estimate acetic acid by its specific gravity. He might confound an acid of 54·5 per cent. with the absolutely anhydrous body, both having the same density. Alcohol and acetic acid are mutual solvents, each dissolving in the other with great readiness; and the latter, like the former, taking up many resinous bodies—gum resins, essential oils, and camphor.

Acetates are derived by the displacement of hydrogen from acetic acid by a basylous radical. Most acetates are soluble in water and alcohol, and are inclined to be deliquescent; they are chiefly prepared by dissolving metallic oxides or carbonates in acetic acid. All acetates are decomposed by a red heat; the alkaline acetates yielding marsh gas, especially in presence of an excess of alkali:—

$$NaC_2H_3O_2 + NaHO = Na_2CO_3 + CH_4.$$

Acetates of earthy metals, on the other hand, when heated, evolve the characteristic odour of acetone, and leave a residue of carbonate, thus:—

$$Ba(C_2H_3O_2)_2 = BaCO_3 + C_3H_6O.$$

Acetates of easily reducible metals, such as copper, yield, when heated, a distillate of acetic acid, leaving a residue of the metal, or, in some cases, of the oxide.

(*For detection and separation of Acetates, see Author's* **Analytical Chemistry**, page 74.)

AMMONIUM ACETATE (SYNS. *Ammoniæ Acetas.* [*In solution*] *Spiritus Mindereri*). **Formula, $NH_4C_2H_3O_2$. Molecular Weight, 77.**

Is produced by dissolving the official **ammonium carbonate** in **acetic acid**, to which it is added until a neutral solution results.

$$N_4H_{16}C_3O_8 + 4HC_2H_3O_2 = 4NH_4C_2H_3O_2 + 3CO_2 + 2H_2O.$$

A solution of ammonium acetate is official under the designation of *liquor ammoniæ acetatis*, and is prepared by neutralizing 10 fluid ounces of acetic acid with a sufficiency of ammonium carbonate, and then adding 2½ pints of water.

This solution decomposes by keeping, becoming alkaline owing to production of **ammonium hydrate** and **ammonium diacetate**, $NH_4C_2H_3O_2.HC_2H_3O_2$. This latter body may also be formed, as a white sublimate, on subjecting a mixture of ammonium chloride and sodium acetate to sublimation.

SODIUM ACETATE (SYN. *Sodæ Acetas*). **Formula, $NaC_2H_3O_2$. Molecular Weight, 82.**

Is formed in the manufacture of acetic acid. If desired pure, it may be produced by the solution of sodium carbonate in acetic acid, or by the action of sodium sulphate upon calcium acetate. Water at 120° F. dissolves about 60 per cent. of sodium acetate, which is usually met with in transparent colourless crystals, soluble in water, forming a solution neutral to test-paper.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 107.)

POTASSIUM ACETATE (SYN. *Potassæ Acetas*). **Formula, $KC_2H_3O_2$. Molecular Weight, 98.**

Is occasionally a bye-product in the preparation of the acid. Is contained in some vegetable secretions, and may be formed in the same manner as sodium acetate. The reaction occurring in the manufacture, is:—

$$K_2CO_3 + 2HC_2H_3O_2 = 2KC_2H_3O_2 + CO_2 + H_2O.$$

It undergoes fusion when heated to incipient redness, and is very deliquescent.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 107.)

It is employed as a precipitant for tartaric acid, with which it produces potassium hydrogen-tartrate and acetic acid, in which the tartrate is insoluble.

Potassium acetate being readily soluble in alcohol, whilst potassium hydrogen-tartrate is insoluble, the addition of that body promotes the success of the test. It is the fused salt which is official, and it is met with in foliaceous satiny masses, very deliquescent, neutral to test-paper, and entirely soluble in rectified spirit.

ARGENTIC ACETATE (SYN. *Acetate of Silver*). **Formula, $AgC_2H_3O_2$. Molecular Weight, 167.**

A white precipitate produced by the addition of argentic nitrate to sodium acetate. It is soluble in acids and ammonium hydrate, likewise in excess of cold water.

CALCIUM ACETATE (SYN. *Acetate of Lime*). **Formula, $Ca2C_2H_3O_2$. Molecular Weight, 158.**

Procured in the purification of pyroligneous acid; but the pure salt is obtained by the neutralization of acetic acid with calcium carbonate, and evaporation to the crystallizing point. It is soluble in alcohol as well as water, and leaves calcium carbonate on being subjected to heat.

ZINC ACETATE (SYN. *Zinci Acetas*). **Formula, $Zn2C_2H_3O_2$. Molecular Weight, 183.**

Produced by the solution of the official **zinc carbonate in acetic acid.** The equation represents that,

$$ZnCO_3.(Zn2HO)_2.H_2O + 6HC_2H_3O_2 = 3Zn2C_2H_3O_2 + CO_2 + 6H_2O.$$

This salt is in thin translucent and colourless crystalline plates of a pearly lustre, with a sharp unpleasant taste. It contains two molecules of water of crystallization, and thus is $Zn2C_2H_3O_2.2H_2O$. By heating to 212° F., the water is driven off, leaving a solid mass, from which, at 380° F., anhydrous zinc acetate sublimes in scaly crystals. A strong heat chars the product.

Zinc acetate is occasionally formed from the metal.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 107.)

CUPRIC ACETATE (SYNS. *Cupri Acetas. Copper Verditer. Crystallised Verdigris*). **Formula, $Cu2C_2H_3O_2$. Molecular Weight, 181·5.**

This salt results from the solution of **cupric oxide** or carbonate, in strong **acetic acid**, and crystallizes out on cooling. The reaction is:—

$$CuO + 2HC_2H_3O_2 = Cu2C_2H_3O_2 + H_2O.$$

When plumbic acetate is added to a solution of cupric sulphate, plumbic sulphate is precipitated, and cupric acetate remains in solution. As solution of cupric acetate cannot be evaporated without undergoing decomposition, the mixed solutions must be filtered whilst hot, and sufficiently strong to deposit the acetate on cooling.

The Pharmacopœia employs *green verdigris*, cupric oxy acetate, sometimes termed sub-acetate of copper, $(Cu_2O)2C_2H_3O_2$, for the purpose of preparing cupric acetate. The reaction is represented as taking place thus:—

$$(Cu_2O)2C_2H_3O_2 + 2HC_2H_3O_2 = 2Cu2C_2H_3O_2 + H_2O.$$

The solution of cupric acetate is employed by the B.P. to detect the butyric acid in zinc valerianate, by distilling with sulphuric acid and adding the acetate to the distillate, when an immediate precipitate or opalescence is

produced in the presence of butyric acid; while valerianic acid does not cause any change for some little time.

If dry cupric acetate be heated until no more acid fumes are liberated, and the temperature be raised to 520° F., cuprous acetate sublimes in white fumes, condensing in flakes of the same colour, which by the action of water form yellow cuprous hydrate and a solution of the cupric acetate.

CUPRIC OXY-ACETATE (SYNS. *Sub-Acetate of Copper. Green Verdigris. Ærugo*). **Formula, $(Cu_2O)2C_2H_3O_2$. Molecular Weight, 261.**

It results from the action of the air upon copper plates moistened with acetic acid in the form of vinegar. In Sweden, the plates are arranged on cloths moistened with vinegar, and the neutral, or rather normal, salt produced is made to take up more of the cupric oxide by exposure to atmospheric action and moisture. It is bright green in colour, insoluble in water, and when heated with sulphuric acid gives off the smell of vinegar, and forms cupric sulphate in solution.

CUPRIC ACETO-ARSENITE, OR (MORE PROPERLY)

CUPRIC ACETO-MET-ARSENITE. Formula, $Cu(C_2H_3O_2)_2.3Cu(AsO_2)$.

This compound is manufactured, under the name of *Schweinfurth, Imperial,* or *Mitis Green,* by acting upon cupric acetate with arsenious acid; also by heating ammonio-cupric sulphate, first with acetic, and then arsenious acid.

Extensively used by painters and others, it has been treated of more appropriately under **Arsenic** (*which see*).

ALUMINIUM ACETATE. Formula, $Al_26C_2H_3O_2$. Molecular Weight, 409.

Is extensively used in dyeing, and is obtained by precipitating aluminium sulphate, or ordinary alum, with plumbic acetate. Also made by dissolving aluminium hydrate in acetic acid. The first process is more generally employed, the reaction being :—

$$3Pb2C_2H_3O_2 + Al_23SO_4 = Al_26C_2H_3O_2 + 3PbSO_4.$$

The solution decomposes by evaporation. The presence of potassium or ammonium sulphate (contained in the alum) does not interfere with the reaction, nor in any way reduce the value of the resulting aluminium acetate.

FERRIC ACETATE (SYNS. *Red Acetate of Iron. Tri-Acetate of Iron*). **Formula, $Fe_26C_2H_3O_2$. Molecular Weight, 466.**

Is produced when any soluble acetate, in neutral solution, is added to ferric chloride which has been shaken with pure moist ferric oxide (or with a slight excess of an alkali), and filtered. It is an uncrystallizable red solid, decomposed by boiling with water, ferric hydrate being precipitated.

The solution thus obtained does not possess the characteristic properties of ferric salts, but gives a brown precipitate (instead of blue) with potassium ferrocyanide. It fails to produce any red colour with potassium sulphocyanide; but the whole of the iron separates in the presence of a little sulphate or phosphate.

It is soluble in alcohol, and the solution is official as *tinctura ferri acetatis*. which is prepared by mixing together spirituous solutions of ferric sulphate and potassium acetate :—

$$Fe_23SO_4 + 6KC_2H_3O_2 = Fe_26C_2H_3O_2 + 3K_2SO_4.$$

This reaction could only take place satisfactorily in the presence of spirit, because potassium sulphate, being insoluble in that menstruum, can be filtered out. The tincture is very apt to spoil by keeping, depositing a basic acetate, and forming acetic ether. This may be altered by the addition of 5 per cent. free acetic acid.

PLUMBIC ACETATE (SYNS. *Plumbi Acetas. Saccharum Saturni. Sugar of Lead*). **Formula, $Pb2C_2H_3O_2.3H_2O$. Molecular Weight, 325.**

Is officially produced by dissolving **plumbic oxide** in dilute **acetic acid**, keeping the latter in excess :—

$$PbO + 2HC_2H_3O_2 = Pb2C_2H_3O_2 + H_2O.$$

The solution is crystallized, taking care that the faint but distinct acid reaction is kept up, and the crystals are dried without heat.

Plumbic acetate is found in white crystalline masses, slightly efflorescent, having an acetous odour and a sweet astringent taste. Its solution in water **feebly reddens litmus, and it also dissolves readily in alcohol.**

(*For analysis, see Author's* **Analytical Chemistry**, *page* 107.)

On the large scale wood vinegar is used in the place of acetic acid, and, instead of oxide, the metal is frequently employed. In this case the neutralization of the acid by the lead occupies some time, as the affinity of the radical of the acid for hydrogen is not sufficiently inferior to its affinity for lead, to enable the latter to expel and replace it. But the lead absorbs oxygen from the air in the presence of an acid, and then transfers it to the hydrogen of that acid, itself combining with the acid radical set free, and plumbic acetate results. The process is practically carried out by placing plates of lead in open vessels containing vinegar. The plates are placed endways; and being of such a length that half may be immersed in the liquid and half may stand above, day by day these are reversed, the end which was immersed in the vinegar one day being exposed to the air the next. This is continued until the whole of the plates are dissolved, and there is no longer any free acid. When this point is obtained, the liquid is evaporated and crystallized.

Solution of plumbic acetate is precipitated slightly on exposure to the air, by absorbing carbonic anhydride; but the acetic acid set free prevents any further action. When heated, it leaves metallic lead, which, if not fused, inflames on being exposed to the air. No effect is produced by the addition of ammonium hydrate to a cold solution of plumbic acetate; and it gives no precipitate with mucilage of acacia (distinction from the oxyacetate).

PLUMBIC OXY-ACETATE (SYNS. *Sub-Acetate of Lead. Saturnine Extract. Goulard's Extract. Plumbi Sub-Acetas*). **Formula, $(Pb_2O)2C_2H_3O_2$. Molecular Weight, 548.**

This compound has not a perfectly definite composition, sometimes containing rather more plumbic oxide than that represented in the formula, and sometimes rather less. It is official in the form of a solution, produced by boiling $3\frac{1}{2}$ ounces of plumbic oxide with 5 ounces of plumbic acetate and 1 pint of water, when the following action results :—

$$PbO + Pb2C_2H_3O_2 = (Pb_2O)2C_2H_3O_2.$$

Liquor plumbi sub-acetatis is a dense, clear, colourless liquid, with alkaline reaction and sweet astringent taste, becoming turbid by exposure to the air; and forming with mucilage of gum arabic an opaque white jelly.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 108.)

The solution, mixed with an equal bulk of alcohol and sufficient water to make eighty times the original volume, is *liquor plumbi sub-acetatis dilutus*, B.P. The alcohol is added with the idea of preservation; but the quantity is too small to be of use, and even if increased would act as little as a preservative. Plumbic oxy-acetate is insoluble in alcohol, consequently the addition of any considerable amount to an aqueous solution would effect its precipitation. By evaporating a solution, with the exclusion of the air, the oxy-acetate separates in needle-like crystals. It is used in analysis for the elimination of colouring and gummy matters from saccharine solutions; for the precipitation of organic acids in the extraction of alkaloids; and as a means of isolating special colouring matters, with a view to their production in a pure condition. In medicine its value depends chiefly upon its power of coagulating mucus. The solution, though strongly alkaline to litmus paper, resembles most true acetates in smelling distinctly of acetic acid.

HYDROGEN PROPIONATE (SYN. *Propionic Acid*). **Formula, $H.C_3H_5O_2$.**

Is usually prepared as potassium propionate by boiling ethyl cyanide (*propionitril*) with potassium hydrate. From this salt the acid may be obtained by distillation with syrupy phosphoric acid. Propionic acid is a colourless liquid, soluble in water, having a specific gravity of ·992, and boiling at 284° F. Most of the propionates are soluble in water.

HYDROGEN BUTYRATE (SYN. **Butyric Acid**). **Formula, $H.C_4H_7O_2$.**

This acid is derived by oxidation from the butyl hydrate, and is contained in butter and in cod liver oil (*oleum morrhuæ*, B.P.). It is, however, usually prepared from sugar or starch, by fermentation with cheese in the presence of calcium carbonate for a month or two, and afterwards digesting the calcium butyrate thus obtained with sulphuric acid. It may be produced in an impure state from butter by saponification with an alkaline hydrate, and distillation with sulphuric acid. It is a clear colourless liquid, burning with a blue flame, and having a mixed odour of vinegar and rancid butter. In its reaction it is powerfully acid. It is capable of solidification by intense cold, and is soluble in water and alcohol in all proportions, boiling at 325° F.

It is detected in valerianates by a process which owes its value to the fact that it causes an immediate precipitation of cupric butyrate when added to cupric acetate, whilst cupric valerianate does not separate for some time.

HYDROGEN VALERIANATE (SYNS. **Valerianic Acid.** *Hydric Valerianate* [Delphinic or Phocinic Acid]). **Formula, $H.C_5H_9O_2$. Molecular Weight, 102.**

Is found in nature in valerian root, and in many plants of the natural order *Compositæ;* also in various secretions and products of animals. When required in a pure state, it is usually procured by distilling sodium valerianate with sulphuric acid.

Valerianic acid is an unpleasant smelling, colourless, acidulous, oily liquid, soluble in alcohol, strong acetic acid, and ether. It dissolves in water to the extent of about three and a half per cent. Boiling point, 347° F.; specific gravity, ·9368 at 60° F. Like all acids derived from alcohols of the methyl series, it is a monad, and forms the salts known as *valerianates*.

(*For detection of Valerianates, see Author's* **Analytical Chemistry**, *page* 75.)

SODIUM VALERIANATE (SYN. *Sodæ Valerianas*). **Formula, $NaC_5H_9O_2$. Molecular Weight, 124.**

Is prepared by distilling fusel oil with a mixture of potassium dichromate and sulphuric acid, neutralizing the distillate with sodium hydrate, evaporating to dryness, and fusing the residue at a gentle heat.

In this process the following reactions occur :—

1. The potassium dichromate and sulphuric acid yield nascent oxygen :—

$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_23SO_4 + 3O_2 + 8H_2O.$$

2. This oxygen converts the amyl hydrate into a mixture of valerianic acid and amyl valerianate :—

$$3C_5H_{11}HO + 2O_2 = HC_5H_9O_2 + C_5H_{11}C_5H_9O_2 + 3H_2O.$$

3. The distillate thus obtained, on neutralizing with sodium hydrate, produces sodium valerianate and re-forms some amyl hydrate :—

$$HC_5H_9O_2 + C_5H_{11}C_5H_9O_2 + 2NaHO = 2NaC_5H_9O_2 + C_5H_{11}HO + H_2O.$$

Commercial sodium valerianate is met with in dry white masses without alkaline reaction, entirely soluble in rectified spirit, and giving out a powerful odour of valerian on the addition of diluted sulphuric acid.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 108.)

It is very deliquescent, but can be obtained in crystalline masses by the spontaneous evaporation of a solution in dry air, at 90° F. The fusing point of the anhydrous salt is 284° F.

This salt affords the best means of procuring the other valerianates, as almost all of them can be precipitated or crystallized out by evaporation, after the addition of a soluble salt of the required metal, to sodium valerianate

Argentic, mercuric, and ferric valerianates can be precipitated by mixing strong solutions of mercuric or ferric chloride, or argentic nitrate, with a saturated solution of sodium valerianate.

ZINC VALERIANATE (SYN. *Zinci Valerianas*). **Formula, $Zn2C_5H_9O_2$. Molecular Weight, 267.**

Is produced by mixing together solutions of zinc sulphate and sodium valerianate, and crystallizing. The reaction is :—

$$ZnSO_4 + 2NaC_5H_9O_2 = Zn2C_5H_9O_2 + Na_2SO_4.$$

Sodium sulphate, being more soluble than the zinc valerianate, remains in the mother liquor.

The product is in brilliant white pearly tabular crystals, with a perceptible odour of valerianic acid, and a metallic taste; scarcely soluble in cold water or in ether, soluble in hot water and alcohol.

It is soluble in ether, and may be produced by the solution of the metal in valerianic acid.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 108.)

CUPRIC VALERIANATE (SYN. *Cupri Valerianas*). **Formula, $Cu2C_5H_9O_2$. Molecular Weight, 265·5.**

Is the only precipitate formed in testing zinc valerianate for butyric acid It forms a solid hydrate if left in contact with water for a short time Though insoluble in acetic acid, it is dissolved by pure water and alcohol. The equation would appear to be :—

$$Cu2C_2H_3O_2 + 2HC_5H_9O_2 = Cu2C_5H_9O_2 + 2HC_2H_3O_2.$$

BISMUTHOUS VALERIANATE (SYN. *Valerianate of Bismuth*). **Formula, $Bi3C_5H_9O_2$.**

Has been occasionally used in medicine. It is produced by mixing sodium valerianate and bismuthous nitrate in strong solutions. The precipitate must only be washed slightly, as, being soluble in water to some extent, it would dissolve if not carefully treated.

HYDROGEN CAPROATE (SYN. *Caproic Acid*). **Formula, $H.C_6H_{11}O_2$.**

Exists as a glyceride in cocoa-nut oil and in butter, from which it may be obtained by saponification with soda, and distilling the soap with tartaric or dilute sulphuric acid. It may also be obtained from amyl cyanide (*capronitril*) and potassium hydrate. It is an oily liquid with a pungent odour, boiling at 400° F.

HYDROGEN ŒNANTHYLATE (SYN. *Œnanthylic Acid*). **Formula, $H.C_7H_{13}O_2$.**

May be obtained by the oxidation of castor oil with nitric acid, or by one of the general processes. It is a colourless oil with a fishy odour, boiling at 455° F., and insoluble in water.

HYDROGEN CAPRYLATE (SYN. *Caprylic Acid*). **Formula, $H.C_8H_{15}O_2$.**

Exists like caproic acid as a glyceride in butter and cocoa-nut oil, and may be similarly prepared. The mixed acids having been neutralized with barium hydrate, are submitted to fractional crystallization, when the barium caprylate crystallizes out first. Below 50° F. it is a solid fat.

HYDROGEN PELARGONATE (SYNS. *Pelargonic Acid. Œnanthic Acid*). **Formula, $H.C_9H_{17}O_2$.**

Exists ready formed in geranium leaves, and is obtained by the action of nitric acid on oil of *rue*. Its ethyl salt is commonly known as œnanthic ether, or *essence of cognac*, being used to give flavour to British brandy and artificial wines. This ether is prepared by dissolving pelargonic acid in strong alcohol, and passing hydrochloric acid gas through the solution, and is also obtained from wine lees by distillation.

HYDROGEN RUTATE (SYNS. *Rutic Acid. Capric Acid*). **Formula, $H.C_{10}H_{19}O_2$.**

Exists as a glyceride in butter and cocoa-nut oil, and also in the fusel oil of Scotch whisky. It is a solid, melting at about 85° F.

HYDROGEN LAURATE (SYN. *Lauric Acid*). **Formula, $H.C_{12}H_{23}O_2$.**

Exists as a glyceride in the fat of bay berries.

HYDROGEN MYRISTATE (SYN. *Myristic Acid*). **Formula, $H.C_{14}H_{27}O_2$.**

Occurs as a glyceride in *oleum myristicæ expressum*, which is known as *myristin*, $C_3H_5 3C_{14}H_{27}O_2$, and from which the acid may be obtained by saponification.

HYDROGEN PALMITATE (SYN. *Palmitic Acid*). **Formula, $H.C_{16}H_{31}O_2$.**

Is derived by oxidation from cetyl hydrate, and is practically produced by heating the residual potassium palmitate left in the retort after the manufac-

ture of cetyl hydrate, with sulphuric acid. It is an odourless, tasteless, white solid, melting at 144° F. As the above process is too expensive for practical use, the customary mode of isolation is to boil palm oil with alcohol so as to extract the more fluid portions, and afterwards to treat the insoluble portion with sodium hydrate. The soap thus produced must be heated with dilute hydrochloric acid. Another method of great interest, both practically and theoretically, is to fuse oleic acid with a saturated solution of sodium hydrate. By this means sodium acetate and palmitate are conjointly formed. Palmitic acid is taken up readily by ether, slightly by alcohol, and not at all by water.

HYDROGEN STEARATE (SYN. **Stearic Acid**). **Formula, $H.C_{18}H_{35}O_2$.**

This acid, which exists in the majority of solid fatty bodies, is best prepared by the saponification of vegetable tallow with potassium hydrate, evaporating to dryness, and treating the residue several times in succession with strong alcohol. The dry potassium stearate, when decomposed with dilute sulphuric acid, yields stearic acid and potassium chloride.

Thus prepared, stearic acid is a solid, white, fatty substance. Its melting point is 156° F., the point of solidification 150° F. Many fatty acids, fatty salts, and other bodies exhibit this curious discrepancy, seeming to require a strong internal force to reduce the molecules to their original state of aggregation. A careful distinction must be made between **stearin** and *stearine*. The former contains glyceryl, and is a salt; the latter is the **commercial** name for impure stearic acid, containing some palmitic acid, obtained by the action of sulphuric acid upon palm oil, which fuses at 140° F. and commences to solidify at 131° F. Stearic acid and stearates exhibit less readiness of fusion than other similar substances.

Sometimes soaps are prepared from the fatty acids, and sometimes from the fats themselves. The "white curd soap" of commerce is tolerably pure sodium stearate, being prepared chiefly from tallow (which contains little oleic acid), by saponification with caustic soda, and then adding salt, which causes the soap to float on the top of the liquid, so that it can be skimmed off.

Sapo animalis is a soap having a white or very light greyish tint; dry; nearly inodorous; horny and pulverizable when kept in dry warm air. Easily moulded when heated. Soluble in rectified spirit. Soluble also in hot water, the solution being neutral or only slightly alkaline to test-paper. It does not impart a greasy stain to paper.

This soap may with advantage be substituted for the hard soap made with olive oil in preparing the *linimentum potassii iodidi cum sapone.*

(*For detection of Stearic Acid and Stearates, see Author's* **Analytical Chemistry**, *page* 75.)

ARACHIDIC ACID. Formula, $H.C_{20}H_{39}O_2$.

Exists as a glyceride in ground-nut oil, and may be obtained by the saponification of that fat. It is a solid fatty acid, melting at 167° F.

CEROTIC ACID. Formula, $H.C_{27}H_{53}O_2$.

Exists in beeswax as ceryl cerotate, or *cerin* (which see). It melts at 172° F.

MELISSIC ACID. Formula, $H.C_{30}H_{59}O_2$.

Is similar to cerotic acid, but melts at 192° F., and is the highest known member of the fatty series.

II. ACIDS OF THE SERIES $C_nH_{2n-2}O_2$.

This series commences with acrylic acid, $H.C_3H_3O_2$, but the only member interesting to us, is,—

HYDROGEN OLEATE (SYN. **Oleic Acid**). **Formula, $H.C_{18}H_{33}O_2$.**

Is separated by pressure from the fatty cake which distils over in the preparation of stearic acid and glycerin. Oleates of the monad metals dissolve in alcohol, but those of the metals of higher atomicity do not. It is obtained in a pure state by the saponification of almond (or olive) oil with alcoholic potassium hydrate; precipitation of the nearly neutralized solution with plumbic acetate, drying the insoluble lead soap thus obtained, and digestion in ether. Pure plumbic oleate dissolves, leaving the other lead salts insoluble. This oleate, after careful decantation, is mixed with hydrochloric acid, filtered, and water added. The oleic acid is precipitated, and the ether and water may be removed by evaporation.

Pure oleic acid is white and solid, below 57° F., when crystallized from alcohol. When, however, it is in the liquid state, it does not solidify above 39° F. Has a neutral reaction, is tasteless and odourless, and is capable of being distilled *in vacuo* without decomposition. Bile, which is alkaline, dissolves it, and forms a soap with a strongly acid reaction. It dissolves in ether, and in cold concentrated sulphuric acid, without alteration; but is not soluble in water. It takes up solid fatty acids and salts, forming a mixture having more or less nearly the consistence of the predominant ingredient. When in the liquid state, it absorbs oxygen to a greater or less extent according to the temperature. *Elaidic acid* is an isomer produced by the action of nitrous acid, and is formed during the manufacture of *unguentum hydrargyri nitratis*, B.P. Oleates contain a monad radical, but they can combine with an excess of oleic acid to form acid *pseuao-salts*. The latter are all liquid, and do not dissolve in water. The neutral salts dissolve in ether and absolute alcohol, without the application of heat. Thus, if a solution of a fat be made in either of these when hot, the stearates and palmitates crystallize out on cooling; the oleates remaining in solution. The oleates of the alkaloids and of metals (the latter salts being generally capable of being made by action upon the oxide or hydrate with oleic acid) are soluble in the natural oleates.

(*For detection of Oleic Acid and Oleates, see Author's* **Analytical Chemistry**, *page* 75.)

AMMONIUM OLEATE (SYNS. *Oleate of Ammonia. Linimentum Ammoniæ*). **Formula, $NH_4C_{18}H_{33}O_2$.**

Is the chief constituent of *linimentum ammoniæ*, B.P.; made by shaking together 1 part by measure of *liquor ammoniæ* and 3 parts of olive oil. When anhydrous it is transparent and gelatinous.

SODIUM OLEATE (SYNS. *Sapo Durus. Oleate of Soda. Oil Soap*). **Formula, $NaC_{18}H_{33}O_2$.**

Is prepared in an impure form as hard soap by boiling together sodium hydrate and oil with a small quantity of water, until saponified. To this solution sodium chloride is then added, which causes the soap to separate and float to the surface, when it is skimmed off, pressed, and moulded. The B.P. states that *sapo durus* should be greyish-white, dry, inodorous; horny and

pulverizable when kept in dry warm air; easily moulded when heated. Soluble in water and also in rectified spirit, not imparting an oily stain to paper. Incinerated, it yields an ash which does not deliquesce.

A solution of sodium oleate in rectified spirit constitutes B.P. *linimentum saponis*, which is directed to be made at a temperature not exceeding 70° F. This instruction is necessary, because at higher temperatures the palmitates and stearates contained in the "hard soap" dissolve also; and the solution, after standing some time at the temperature of air, especially in cold weather, deposits these bodies, thus causing the solution to gelatinize. The so-called transparent glycerine soap, is sodium soap which has been dissolved in spirit.

POTASSIUM OLEATE (SYNS. *Sapo Mollis. Oleate of Potash. Oleic Potash Soap*). **Formula, $KC_{18}H_{33}O_2$.**

Is obtained in the pure condition by substituting potassium for sodium hydrate in the preparation of the last-mentioned soap. It may be made in an impure state by the action of potassium hydrate on olive oil. This is the B.P. process.

Soft soap is very deliquescent and soluble in water. A solution of 25 per cent. strength (the strongest procurable) forms a very thick liquid, yielding, on dilution, a gelatinous solid, which, when dissolved in alcohol, exhibits an acid reaction.

Sodium soap may be precipitated from a solution by the addition of sodium chloride, while potassium soap cannot, and soft soap, therefore, always contains glycerin. Both sodium and potassium oleates may be obtained free from glycerin by digesting well washed *lead plaster* with a strong solution of sodium or potassium carbonate on a water bath.

CALCIUM OLEATE (SYNS. *Oleate of Lime. Linimentum Calcis*). **Formula, $Ca2C_{18}H_{33}O_2$.**

Is produced by the addition of any oleate, soluble in water, to a salt of calcium, such as calcium chloride or hydrate:—

$$2KC_{18}H_{33}O_2 + Ca2HO = Ca2C_{18}H_{33}O_2 + 2KHO.$$

It is insoluble in water, but soluble in weak hot alcohol.

The B.P. calcium soap, *linimentum calcis*, is made with olive oil and solution of calcium hydrate, and consequently contains glycerin and a large excess of oil. In fact, the amount of calcium hydrate contained in the prescribed quantity of *liquor calcis* is only $1\frac{1}{2}$ grains, and that being added to 2 ounces of olive oil, forms a liniment containing considerably less than 1 per cent. of true calcium oleate.

PLUMBIC OLEATE (SYN. *Oleate of Lead*). **Formula, $Pb2C_{18}H_{33}O_2$.**

Is produced, in an impure state, by the action of plumbic oxide on olive oil in the presence of hot water. The reaction is somewhat as follows:—

$$2(C_3H_53C_{18}H_{33}O_2) + 3PbO + 3H_2O = 3Pb2C_{18}H_{33}O_2 + 2C_3H_53HO.$$

(Glyceryl Trioleate.) (Plumbic Oleate.) (Glyceryl Hydrate, or Glycerin.)

The B.P. directs:—

Take of

Oxide of Lead, in fine powder	4 pounds.
Olive Oil	1 gallon.
Water	$3\frac{1}{2}$ pints.

Boil all the ingredients together gently by the heat of a steam bath, and keep them simmering for four or five hours, stirring constantly until the product acquires a proper consistence for a plaster, and adding more water during the process if necessary.

The plumbic oleate thus prepared is liable to contain stearate. Hence, for estimation, and for the purpose of procuring a pure sample, it must be carefully dried until absolutely free from moisture, digested with boiling anhydrous ether, and the solution filtered whilst hot. Plumbic oleate crystallizes out on cooling, and if it be recrystallized until a white powder is obtained, this melts to a yellow liquid when heated to about 180° F. It is soluble in oil of turpentine, and by exposure to the air when fused becomes gelatinous.

III. DIATOMIC ACIDS.

The diatomic alcohols possess the power of forming two acids by successive stages of oxidation. For example, it was found that glycol could form both glycollic and oxalic acids, the former monobasic and the latter bibasic (*see equations, page* 231). Of the monobasic series, commencing with glycollic acid, we have only one member of interest, viz.: lactic acid; but of the bibasic series, commencing with oxalic acid, we have several which require close study.

HYDROGEN LACTATE (SYN. **Lactic Acid**). **Formula, $HC_3H_5O_3$.**

Is obtained from many carbon compounds when subjected to the action of a suitable ferment, and also exists in sour milk, from which it was first formed, and to which it owes its name. Many animal secretions contain it, notably the gastric juice. It is formed before butyric acid in the fermentation of a mixture of a solution of glucose (produced from cane or ordinary sugar by heating for a short time with tartaric acid), calcium carbonate (chalk) and milk, with cheese which is in an advanced state of decomposition, at 86° to 95° F. The time required for the conversion is about a week, and the best proportions are 24 of sugar, 12 of calcium carbonate, 1 of cheese, and 100 of water. After some days a thick crystalline paste is produced. The process should be continued until the mass begins to *thin* slightly, owing to the transformation of a little calcium lactate into calcium butyrate, which is more soluble in water. A small quantity of water and calcium oxide is then added, and the whole is boiled for an hour, strained, and evaporated. The crystals, which separate after three or four days, are washed with a very little cold water, and dissolved in hot water, and decomposed by sulphuric acid, cautiously avoiding excess. This conversion of sugar into lactic acid is called the *lactic fermentation*, and takes place spontaneously in milk. Working with ordinary sugar no gain or loss in weight takes place, but with milk sugar the elements of water are assimilated thus :—

$$C_{12}H_{22}O_{11} + H_2O = 4HC_3H_5O_3.$$

Lactic acid is a clear, odourless liquid, having somewhat the appearance of glycerin. It is a strong acid, liberating hydrogen when brought in contact with zinc or magnesium, and forming lactates of those metals; distils when heated with partial decomposition; and is soluble in alcohol, ether, and water.

On account of its normal presence in the healthy stomach, it is administered either alone or in combination with the digestive ferment pepsin, in cases where an insufficiency is suspected. Lactic acid, having an affinity for water, absorbs atmospheric moisture, and does not solidify when reduced in tem-

perature to 45° F. When heated with an excess of strong sulphuric acid, pure carbonous oxide (to the extent of more than 30 per cent. of the lactic acid taken) is evolved. A variety of lactic acid, contained in muscular tissue, has been termed from its derivation *sarco lactic acid*. By heating to 270° to 290° F. for some hours, it yields the ordinary acid on solution in water. The general method for the preparation of lactates is the solution of the metal or carbonate in the acid. In some instances double decomposition of sodium or *ammonium lactate* by a soluble salt of the metal is the better process. Lactic acid, which is a monad, can only in theory form neutral salts; but owing to the affinity of lactates for an excess of lactic acid, compounds can be formed which are not truly acid salts, but are similar to the so-called potassium diacetate, $KC_2H_3O_2.HC_2H_3O_2$.

The only general properties of importance in **lactates** are the slight degree in which they dissolve in cold water, their spontaneous separation from their solutions when exposed to the air at ordinary temperatures, and the insolubility of all (except *hydrogen lactate*) in ether.

(*For detection of Lactic Acid and Lactates, see Author's* **Analytical Chemistry**, *page* 76.)

ARGENTIC LACTATE (SYN. *Lactate of Silver*). **Formula, $AgC_3H_5O_3$.**

This salt is made by the solution of argentic carbonate in boiling lactic acid. When a solution of this salt is boiled for some hours, a dark flocculent precipitate separates, and the liquid after subsidence has a blue colour. The acid to be used should be pure, and may be obtained from any lactate by the addition of a quantity of sulphuric acid not sufficient to completely decompose it, shaking with ether, filtering, and evaporating.

ZINC LACTATE (SYN. *Lactate of Zinc*). **Formula, $Zn2C_3H_5O_3$.**

Is occasionally used in medicine, and, for that purpose, may be prepared in a pure condition by dissolving zinc carbonate in the acid:—

$$ZnCO_3 + 2HC_3H_5O_3 = Zn2C_3H_5O_3 + CO_2 + H_2O.$$

MERCUROUS LACTATE (SYNS. *Sub-Lactate of Mercury. Lactate of Mercury*). **Formula, $Hg_22C_3H_5O_3$.**

When solutions of potassium or sodium lactate and mercurous nitrate, in boiling water, are mixed, crystals of a splendid crimson or pink hue are deposited on cooling, which form the above named salt. It is of no practical importance, except as a confirmatory test if a considerable quantity of pure lactic acid can be isolated, as described under **Argentic Lactate.**

FERROUS LACTATE (SYN. *Proto-Lactate of Iron*). **Formula, $Fe2C_3H_5O_3$.**

This salt, which results from the solution of metallic iron in dilute lactic acid, is sometimes employed in medicine, especially on the Continent. Its crystals are clear, with a faint green tint, and are not readily oxidizable, even when in solution.

HYDROGEN OXALATE (SYN. **Oxalic Acid**). **Formula, $H_2C_2O_4 2H_2O$. Molecular Weight, 126.**

Exists in nature as *potassium quadroxalate*, or *salt of sorrel*, in rhubarb, *Rumex Acetosa*, and *R. Acetosella*, but is usually prepared by the **oxidation** of a **carbohydrate**, such as starch, sugar, or cellulose.

Oxalic acid was formerly made by the decomposition of sugar by nitric acid. 1 part of sugar is heated gradually with 7 parts of nitric acid, B.P., and 1 part of water, to 212° F. When the action has ceased, the solution is evaporated to the crystallizing point. As the crystals are liable to hold nitric acid in mechanical combination, it is advisable to expose them to dry air, upon which efflorescence occurs, and a slight degree of heat will drive off most of this impurity. The crystals must be redissolved, and still further purified by recrystallization. It is occasionally necessary to repeat this process several times, after each of which it is as well to test the freedom of the crystals from the acid in question.

The sugar method is now seldom adopted, and the following process is the best practical one at present known :—1 part of sawdust, starch, or almost any non-nitrogenous carbonaceous matter, is mixed with a solution, in the least possible quantity of water, of 2 parts of potassium hydrate and 1 part of sodium hydrate. A shallow iron dish is coated to a depth of some inches with the pasty mass, and then submitted to a heat between 240° and 500° F., being kept below the latter temperature for two or three hours. The heat is then lowered gradually, five or six hours elapsing before it comes down to 300° F.; after which it may be removed from the source of heat, and when cold treated with a little water at the ordinary temperature. This dissolves the excess of hydrate, etc.; but as the oxalate which is produced is not very soluble, it is not affected. The dry cake upon the dish may contain 30 per cent. of oxalic acid. The alkaline oxalate thus produced is boiled with calcium hydrate and water, calcium oxalate being precipitated. The calcium oxalate is washed, decomposed with sulphuric acid, and the clear solution, obtained by filtration, evaporated nearly to the crystallizing point, when, if any calcium sulphate separates, it must be filtered, and the evaporation continued till crystals are obtained on cooling.

Oxalic acid occurs in colourless crystals, greatly varying in size, and having the formula, $H_2C_2O_4.2H_2O$. It is a strong acid, very poisonous, and readily dissolving in water and alcohol; and entirely dissipated by a heat below 350°.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 108.)

The pure acid does not stain; but the samples occurring in commerce sometimes colour paper yellow, through containing nitric acid, which can be detected by making a strong solution and adding to it a crystal of ferrous sulphate, when a brown or purple coloration shows the presence of nitric acid. Boiling a few crystals with an extremely dilute solution of indigo sulphate will also serve as a test, nitric acid discharging the colour.

Water, at the ordinary heat of 60° F., dissolves 12·5 per cent. of oxalic acid; alcohol, under the same circumstances, takes up 25 per cent.; and in boiling water it is soluble to the extent of 100 per cent. Contamination with nitric acid greatly increases the readiness and extent of its solubility.

After its water of crystallization has been expelled at 212° F., oxalic acid can be sublimed at 320° F. in crystals which are anhydrous; but more or less decomposition invariably takes place. It is not oxidized by strong nitric acid, except upon long boiling.

A property of oxalic acid which is found valuable in analysis, is its rapid and perfect oxidation when treated with manganic dioxide or potassium permanganate and sulphuric acid. It is also readily oxidized by chlorine when moist or in solution. It constitutes a test for gold, in consequence of its power of precipitating that metal from auric chloride.

Oxalic acid decomposes chlorides like sulphuric acid; and, when added to cupric sulphate in solution, displaces the sulphuric acid, which enters into solution, cupric oxalate being thrown down.

Oxalic acid behaves as a dyad, and forms neutral and acid salts, termed **oxalates**, having the following characteristics in common.

1. Those of the alkalies are soluble in water, the neutral salts, however, more readily than the acid salts. The others dissolve in dilute mineral acids, but not in acetic acid.

2. All oxalates yield carbonous oxide by heat. Those whose carbonates are easily decomposed by that force, leave oxides, and evolve carbonic anhydride as well as carbonous oxide; whilst those whose carbonates are tolerably stable, such as potassium and sodium, and in some cases (when the heat is not above dull redness) calcium, barium, and strontium, leave the metal as carbonate.

3. Oxalates, in which the metal is one which is readily reduced, give off carbonic anhydride only, thus:—

$$Ag_2C_2O_4 = Ag_2 + 2CO_2.$$

The plumbic oxalate is peculiar, giving, when heated in a closed vessel, plumbous oxide (Pb_2O).

4. Heated with sulphuric acid, they give, without exception, carbonous oxide and carbonic anhydride, a sulphate remaining, and no blackening taking place.

(*For detection of Oxalic Acid and Oxalates, see* **Author's Analytical Chemistry**, *page* 76.)

AMMONIUM OXALATE (SYNS. *Ammonic Oxalate. Oxalate of Ammonia*).
Formula, $(NH_4)_2C_2O_4.2H_2O$.

Is produced by neutralizing oxalic acid with ammonium carbonate, the latter being added until the solution does not affect neutral litmus paper:—

$$2H_2C_2O_4 + N_4H_{16}C_3O_8 = 2(NH_4)_2C_2O_4 + 3CO_2 + 2H_2O.$$

It crystallizes in long colourless rhombic prisms, soluble in cold water but much more soluble in boiling water. When dried at 212° F. and heated, it gives off water and yields a sublimate of oxamide. (*See* **Amides.**)

(*For analysis, see Author's* **Analytical Chemistry**, *page* 108.)

This substance is of importance as a reagent in analysis, being employed for the detection of calcium. It is formed spontaneously in solutions of cyanogen, by the combination of that body with water, thus:—

$$C_2N_2 + 4H_2O = (NH_4)_2C_2O_4.$$

When distilled with phosphoric anhydride, ammonium oxalate gives up $4H_2O$, and forms cyanogen among other products.

AMMONIUM HYDROGEN OXALATE (SYN. *Binoxalate of Ammonia*).
Formula, $NH_4HC_2O_4.H_2O$.

Is less soluble that the normal oxalate, and when heated to 450° F. gives up a molecule of water and yields oxamic acid. (*See* **Amides.**)

SODIUM OXALATE (SYNS. *Oxalate of Soda. Sodic Oxalate*).
Formula, $Na_2C_2O_4$.

Results from the crude ingredients used in the manufacture of the acid, and is not otherwise interesting.

POTASSIUM DIOXALATE (Syns. *Binoxalate of Potash. Salt of Sorrel*). **Formula, $KHC_2O_4.2H_2O$.**

Is obtained in Switzerland by treating the juice of the plants mentioned under oxalic acid, and also of some members of the species *Oxalis*, with albuminous matter, or clay, for the purpose of removing the colouring and similar matters, and then evaporating the clarified solution until the potassium dioxalate separates out on cooling. A mixture of this, or the following salt, with citric acid, is employed to remove ink-stains from linen, under the designation of *salts of lemon*. From the power it possesses of dissolving metallic oxides, it is commonly used to polish copper, brass, etc.

POTASSIUM QUADR-OXALATE (Syns. *Salt of Sorrel. Potassium Tetr-Oxalate*). **Formula, $KHC_2O_4.H_2C_2O_42H_2O$.**

Is sometimes met with under the title of "salt of sorrel," so that it is probable that some plants owe their acid taste to this salt as well as to that just described. It may be substituted for the dioxalate for all practical purposes. It is about twice as soluble in cold water as the preceding salt.

CALCIUM OXALATE (Syns. *Calcic Oxalate. Oxalate of Lime*). **Formula, CaC_2O_4.**

Is contained as *raphides* in rhubarb and other plants, and is extensively produced in lichens growing on various kinds of limestones. It is the form in which both oxalic acid and calcium are precipitated for estimation, and is frequently met with as an urinary deposit, constituting the so-called *mulberry calculus*.

CERIUM OXALATE (Syns. *Cerous Oxalate. Cerii Oxalas*). **Formula, $CeC_2O_4.3H_2O$.**

This salt results from the addition of ammonium oxalate to a soluble salt of cerium. The reaction is: —

$$CeCl_2 + (NH_4)_2C_2O_4 = CeC_2O_4 + 2NH_4Cl.$$

The B.P. describes it to be a white granular powder, insoluble in water, decomposed at a dull red heat into reddish-brown ceric oxide, Ce_2O_3.

The production of this salt is one of the leading tests for cerium.

(*See separation of Cerium and Iron in Author's* **Analytical Chemistry**, *page* 38; *for analysis and impurities of Cerium Oxalate, see ibid., page* 108.)

PLUMBIC OXALATE (Syn. *Oxalate of Lead*). **Formula, PbC_2O_4.**

Is produced on adding any soluble oxalate to plumbic acetate, the reaction being (if we take ammonium oxalate):—

$$(NH_4)_2C_2O_4 + Pb2C_2H_3O_2 = PbC_2O_4 + 2(NH_4)C_2H_3O_2.$$

The most curious property of plumbic oxalate, is that of its leaving plumbous oxide when heated; thus:—

$$2PbC_2O_4 = Pb_2O + 3CO_2 + CO.$$

Plumbic oxalate dissolves in boiling ammonium chloride, and in cold nitric acid, though not in acetic acid.

HYDROGEN SUCCINATE (SYNS. **Succinic Acid.** *Volatile Salt of Amber* [obsolete]). **Formula, $H_2C_4H_4O_4$.**

Exists in amber, in several kinds of turpentine, and a few plants official in the B P ; such as *Artemisia Santonica, Artemisia Absinthium, Lactuca virosa.*

Succinic acid is frequently prepared either from butyric acid by the oxidizing action of nitric acid, or from malic or tartaric acids by the deoxidizing effect of hydriodic acid. With malic acid the reaction is :—

$$\underset{\text{(Malic Acid.)}}{H_2C_4H_4O_5} + 2HI = H_2C_4H_4O_4 + I_2 + H_2O.$$

With tartaric acid, more hydriodic acid must be employed ; thus,—

$$\underset{\text{(Tartaric Acid.)}}{H_2C_4H_4O_6} + 4HI = H_2C_4H_4O_4 + 2I_2 + 2H_2O.$$

Both of these actions may be reversed by suitable means, succinic acid being thus made to produce malic and even tartaric acid

Succinic acid may be produced, in an impure state, from amber, by dry distillation, acetic acid also passing over simultaneously, and, during the whole of the distillation, *volatile oil of amber*. This oil is analogous to that obtained on applying a similar process to other resins. The presence of acetic acid is caused by decomposition. If the watery distillate of mixed acids, which is never free from oily matter, be heated to 212° F., and immediately filtered, impure succinic acid separates in crystals as the temperature becomes lower. A large amount of impure succinic acid likewise crystallizes out on the neck of the retort whilst the dry distillation is in progress. By treating these crystals with nitric acid until they are free from odour, and recrystallizing, the pure acid is obtained.

Succinic acid is a white crystalline solid, differing from lactic acid in being almost insoluble in ether, and only oxidized with difficulty. It is not charred by heating with strong sulphuric acid It is a dyad acid, forming neutral and acid salts. Like neutral lactates, oxalates, and acetates, these can combine with a molecule of acid to form salts analogous to potassium quadr-oxalate.

(*For detection of Succinic Acid and Succinates, see Author's* **Analytical Chemistry**, *page* 76.)

AMMONIUM SUCCINATE (SYN. *Succinate of Ammonia*). **Formula, $(NH_4)_2C_4H_4O_4$.**

Formed by saturating succinic acid with ammonium hydrate, and crystallizing. It is sometimes employed as a means of precipitating iron for estimation, ferric succinate being, unlike most ferric salts, granular, and therefore can be readily freed from foreign matters by washing.

FERRIC SUCCINATE (SYN. *Succinate of Iron*). **Formula, $Fe_23C_4H_4O_4$.**

An insoluble chocolate-coloured salt, produced by the action of the last-named salt on ferric chloride. When digested with ammonium hydrate, ferric hydrate is obtained. The resulting solution of ammonium succinate, when heated and hydrochloric acid added in excess, does not yield crystals on cooling. This is a very useful distinction between ferric benzoate and succinate ; the former, when similarly treated, forms abundant crystals of the but slightly soluble benzoic acid.

IV. TRIATOMIC AND BIBASIC ACIDS.

May be viewed as being formed from the Oxalic series by the substitution of HO for H.

HYDROGEN MALATE (SYN. **Malic Acid**). **Formula,** $H_2C_4H_4O_5$.

Is derived from an alcohol of very little importance, and is contained in most fruits employed for domestic purposes. Unripe apples, mountain ash berries, and rhubarb stalks, are the sources more frequently resorted to for its preparation. The juice of either of these, preferably the second, is expressed, heated to boiling, and calcium carbonate is added till effervescence ceases; the liquid when cold is filtered; plumbic nitrate being added, the liquid is allowed to stand until plumbic malate becomes crystalline. The crystals are dissolved after a few washings with cold water, and sulphuretted hydrogen passed until the liquid smells strongly. Warm gently, filter, boil the filtrate till free from unpleasant odour, and evaporate on a water bath. The syrupy product yields crystals by spontaneous evaporation at about 100° F.

Malic acid is a colourless, inodorous, deliquescent, crystalline acid, very soluble in water and alcohol.

Only two classes of *malates* can be formed, of which the neutral is least stable. *Calcium* malate is soluble in water, *but not in alcohol, even if dilute.* Long boiling causes its separation from a strong slightly acid solution.

Strong sulphuric acid when heated with a pure malate causes charring very slowly, though it does so rapidly with tartaric acid. Plumbic malate undergoes slight solution in dilute acetic and nitric acids, being changed from the powder form in which it is first precipitated to small needle-like crystals. This fact shows that the crystals are not soluble in dilute acids though the amorphous form is. Plumbic malate in the amorphous variety fuses in boiling water.

V. TRIATOMIC AND TRIBASIC ACIDS.

ACONITIC ACID. Formula, $H_3C_6H_3O_6$.

This acid exists in *Aconitum Napellus*, and is also produced by heating citric acid till it fuses and commences to discolour, when it gives up water thus:—

$$H_3C_6H_5O_7 - H_2O = H_3C_6H_3O_6.$$

Aconitic acid is very soluble in water, alcohol, and ether.

HYDROGEN MECONATE (SYN. **Meconic Acid**). **Formula,** $H_3C_7HO_7$.

May be prepared from opium by neutralizing a strong solution (obtained by treatment with water at 100° F.) with calcium carbonate, and after reducing to a small bulk on a water bath, introducing a saturated solution of calcium chloride until no more precipitate is formed. The insoluble matter is calcium dihydrogen meconate, and must be washed and pressed to free it from solid matters. The precipitate is then treated with a little hydrochloric acid and boiling water, when it dissolves, and deposits crystals on cooling. Then, if the crystals be redissolved in hot water, and excess of hydrochloric acid added, meconic acid falls as the liquid cools, being only slightly soluble in water

containing hydrochloric acid. The crystals, which are coloured brown, may be rendered colourless by heating with two parts of water, and adding ammonium hydrate, the temperature being raised until perfect solution ensues. On cooling, the liquid becomes a solid mass. The dark liquid must be entirely pressed out of the crystals, and then these are made to undergo several successive recrystallizations from a saturated solution in hot water. Afterwards, on introducing an excess of hydrochloric acid into a hot solution, the meconic acid is obtained in colourless plates on cooling. The crystals contain 3 molecules of water of crystallization, which, when driven off by heating to 212° F., leave the acid as a white pulverulent mass, soluble, like the crystallized form, in water, alcohol, and ether, and having a decidedly acid reaction. It communicates a red coloration to a solution of ferric chloride on carefully neutralizing the mixed solutions. This colour is neither discharged by mercuric chloride (distinction from thiocyanates) nor by very dilute hydrochloric acid (distinction from acetates). Meconic acid forms three classes of meconates with monad metals, tri-, di-, and mono- metallic. The latter exhibit an acid, the former exhibit a neutral, reaction with litmus.

The hydrogen meconates of these metals are but slightly soluble, and form very small crystals. They may be produced by the neutralization of the acid with a carbonate or hydrate. This is the mode of preparing the mono-hydrogen salts. The di-hydrogen salts may be produced by adding a portion of acid, equal to the first used, to the mono-hydrogen meconates.

Of ammonium, sodium, and potassium meconates, the first has not been prepared, the other two have. The second (sodium) is crystallizable, and the last uncrystallizable.

VI. TETRATOMIC ACIDS.

Are derived from tetratomic alcohols by the substitution of 1, 2, 3, or 4 *atoms* of O for a corresponding number of *molecules* of H.

HYDROGEN TARTRATE (Syns. **Tartaric Acid.** *Acidum Tartaricum. Essential Oil of Tartar* [obsolete]). **Formula, $H_2C_4H_4O_6$. Molecular Weight, 150.**

Exists in many vegetable productions, but is usually procured from potassium hydrogen tartrate which is deposited from grape juice during fermentation. It is found in the free state in tamarinds and very acid fruits; it is even a constituent, though to an extremely small extent, of potatoes.

The usual process for the formation of tartaric acid is by treating potassium hydrogen tartrate (cream of tartar) with calcium carbonate (in the form of chalk or whiting) and boiling water, adding the carbonate until effervescence ceases. The solution is then mixed with calcium chloride until no more precipitate is formed; and the whole having been allowed to settle, the precipitate is washed by decantation with cold water till the washings are tasteless. The precipitated calcium tartrate is then transferred to a basin and boiled with dilute sulphuric acid for half an hour, which forms free tartaric acid and calcium sulphate. The bulk of the latter body having been separated by filtration, the solution is evaporated to a density of 1·21, and cooled, when the remainder of the calcium sulphate separates out, and the clear liquid is then crystallized. The reactions are :—

1. $2KHC_4H_4O_6 + CaCO_3 = K_2C_4H_4O_6 + CaC_4H_4O_6 + CO_2 + H_2O$.
2. $K_2C_4H_4O_6 + CaCl_2 = CaC_4H_4O_6 + 2KCl$.
3. $2CaC_4H_4O_6 + 2H_2SO_4 = 2H_2C_4H_4O_6 + 2CaSO_4$.

Tartaric acid is met with in colourless crystals, the primary form of which is the oblique rhombic prism. It is freely soluble in water and in dilute spirit, insoluble in ether, but soluble in absolute alcohol. The crystals fuse at 340° F., forming *meso*-tartaric acid. At 374° F. it gives up H_2O and becomes tartaric anhydride, $C_8H_8O_{10}$; and at 401° F. it gives off CO_2 and leaves *para*-tartaric acid.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 109.)

The B.P. solution of tartaric acid, which serves as a test for potassium acetate, bromide, and iodide, is made by dissolving 1 part of tartaric acid in 8 parts of water and 2 parts of rectified spirit. The spirit is added as a preservative, the watery solution decomposing on being kept.

Tartaric acid exists in four forms :—

1. *Dextro-tartaric*, or *true tartaric acid.* This is more soluble in alcohol than the other varieties, and the crystals are anhydrous.

2. *Lævo-tartaric acid.* The crystals of this are also anhydrous, but it rotates the plane of polarization of light to the left, the former acid turning it to the right.

3. *Racemic acid*, or *para-tartaric acid*, exists, together with the ordinary acid, in certain grapes cultivated on the borders of the Upper Rhine. When manufactured from these, the racemic acid may be picked out from the ordinary acid by the efflorescence of its crystals. It may be produced from the ordinary acid by heat, is absolutely without effect on polarized light, and may be separated by heat into the former modifications.

4. *Meso-*, or *inactive, tartaric acid* resembles the last named, but is not resolvable into the *dextro* and *lævo* forms by heat. It has no action on light.

The ordinary tartaric acid is sometimes denominated *dextro-racemic acid;* and occasionally contains lævo- and meso-tartaric, and also racemic acids. Tartaric acid does not form any precipitate in solutions of barium, strontium, and calcium chlorides, although it does in solutions of the hydrates of these metals. All potassium salts in tolerably strong solution, form a precipitate on the addition in excess of tartaric acid. The precipitation is much accelerated by stirring, and by the addition of a little alcohol, in which the precipitate (potassium hydrogen-tartrate—cream of tartar) is much less soluble than in water. Small quantities of tartaric acid are best detected by the addition of potassium acetate, and not potassium hydrate or carbonate; because, if the latter be in excess (however slight), potassium tartrate is formed, which is freely soluble in water.

A trifling percentage of tartaric in commercial citric acid may be detected by the addition of rectified spirit and potassium acetate. If tartaric acid be present, microscopic white crystals will separate. This reaction is valuable as a distinctive test for tartaric acid in case of doubt as to whether a sample be this or citric acid.

Tartrates are of three classes, viz.: acid, neutral, and double; the second and third may be formed both with monad and dyad metals (the first with monads only).

With metals which are apparently triad, but really pentad, tartaric acid produces salts in which one atom of a monad metal, one molecule of tartaric acid, and one molecule of oxygen combine to satisfy the five affinities of the metal. Examples are,—

Of the first group, *i.e.*, acid tartrates :—

$KHC_4H_4O_6$.	$NH_4HC_4H_4O_6$.
(Potassium Hydrogen-Tartrate.)	(Ammonium Hydrogen-Tartrate.)

Of the second, *i.e.*, neutral tartrates :—

$K_2C_4H_4O_6$. (Potassium Tartrate.) $CaC_4H_4O_6$. (Calcium Tartrate.)

Of the third, *i.e.*, double tartrates :—

1. Of two monad metals, neither being hydrogen :—

$KNaC_4H_4O_6$. (Potassium Sodium-Tartrate.) $KNH_4C_4H_4O_6$. (Potassium Ammonium-Tartrate.)

2. Of a monad and dyad metal united :—

$K_2Ba2C_4H_4O_6$.
(Potassium Barium-Tartrate, or Bario-Potassium Tartrate.)

3. Of a monad metal and a monad or triad radical derived from a triad-like metal :—

$K(SbO)C_4H_4O_6$. (Potassium Antimonyl Tartrate.) $Na(SbO)C_4H_4O_6$. (Sodium Antimonyl Tartrate.)

The general characters of **tartrates**, are :—

1. Monad metals (except silver) form freely soluble neutral tartrates.

2. The acid salts of the same metals are only slightly soluble, decreasing in readiness of solution in the following order :—

Sodium, Ammonium, Potassium.

3. No tartrates dissolve in alcohol. As it is a rule *that no body can serve as a medium to cause a substance dissolved in it to act upon another which it is incapable of dissolving, if the possible product is also insoluble*, it follows that tartaric acid dissolved in alcohol does not affect potassium carbonate, which is insoluble in that substance, because potassium hydrogen tartrate is also insoluble. The tartrates of the metals which are dyad, triad, etc., are little soluble in water. Dilute acids, such as nitric, hydrochloric, and solution of tartaric (or in very few cases acetic), will dissolve them with tolerable facility. Potassium, sodium, or ammonium hydrates render all tartrates soluble, with the exception of mercuric tartrate, which is insoluble in the three; and argentic tartrate, which is insoluble in the first and second.

(*For detection and separation of Tartaric Acid and Tartrates, see Author's* **Analytical Chemistry**, *page* 77.)

AMMONIUM HYDROGEN-TARTRATE (Syns. *Acid Tartrate of Ammonium. Bitartrate of Ammonia*). **Formula,** $NH_4HC_4H_4O_6$.

Is a white crystalline substance resembling potassium hydrogen-tartrate in other respects besides solubility. It is produced by adding a strong solution of ammonium hydrate to tartaric acid, avoiding excess. The only bye product is water, as will be seen from the equation :—

$$H_2C_4H_4O_6 + NH_4HO = NH_4HC_4H_4O_6 + H_2O.$$

AMMONIUM TARTRATE (Syn. *Tartrate of Ammonia*).
Formula, $(NH_4)_2C_4H_4O_6$.

This salt, which is of little importance, results from the action of tartaric acid upon ammonium carbonate or hydrate. A convenient method is to take two equal portions of a solution of ammonium hydrate; transform one into the last described salt, add the other, agitate, and then evaporate. The crystals which separate (after sufficient concentration) on cooling, are prisms,

which by atmospheric influences become converted into the acid salt, the conversion being attended with efflorescence.

SODIUM HYDROGEN-TARTRATE (SYN. *Bitartrate of Soda*). **Formula, $NaHC_4H_4O_6$.**

Prepared like ammonium hydrogen-tartrate, but is much more soluble. It is occasionally used instead of the acid as a test for potassium.

SODIUM TARTRATE (SYN. *Tartrate of Soda*). **Formula, $Na_2C_4H_4O_6$.**

Obtained by the addition of sodium carbonate to tartaric acid until a neutral solution results, and evaporating.

POTASSIUM HYDROGEN-TARTRATE (SYNS. *Cream of Tartar. Potassæ Tartras Acida. Acid Tartrate of Potash. Bitartrate of Potash. Argol*). **Formula, $KHC_4H_4O_6$. Molecular Weight, 188.**

Exists in grape juice, and is deposited as the fermentation generates alcohol, in consequence of its solubility in that substance being less than in water. The salt is of a reddish colour, and requires to be purified by crystallization. As it dissolves in boiling water to the extent of 1 in 18, and water at 60° F. does not take up more than 1 in 60, a solution made at the former temperature deposits a large proportion on cooling. The crystals (which are very small) differ from those of most substances inasmuch as they float on the mother-liquid (whence the name of "cream of tartar"). The purified salt possesses, according to the B.P., the following characters:—

A gritty white powder, or fragments of cakes crystallized on one surface, of a pleasant acid taste. Sparingly soluble in water; insoluble in spirit. Heated in a crucible, it evolves inflammable gas and the odour of burnt sugar; and leaves a black residue, consisting of potassium carbonate mixed with finely-divided carbon.

(*For analysis and impurities, see Author's* **Analytical Chemistry**, *page* 109.)

It is readily dissolved by potassium hydrate and by nitric, hydrochloric, and sulphuric acids, if not dilute. In the former case potassium tartrate is produced; in the latter, tartaric acid. Mixed with potassium nitrate in equal quantity, and the mixture thrown into a red-hot crucible, deflagration occurs, and a white flux is formed, which when fused with many substances reduces them to a state in which they can be readily dissolved in acids. If, however, only half the weight of potassium nitrate be mixed with the tartrate, and the mixture heated, *black flux* results, which is employed for the purpose of reducing the metal from metallic salts, the finely-divided carbon immediately removing the oxygen contained in them, and the potassium carbonate also present combining with such radicals as chlorine or sulphur. Cream of tartar is also used in dyeing, and is an excellent addition to such dentifrices as are intended to produce whiteness of the teeth.

Ordinary *cream of tartar* always contains calcium tartrate, and has been said to be sometimes adulterated by barium sulphate.

POTASSIUM TARTRATE (SYNS. *Potassæ Tartras. Potassic Tartrate*). **Formula, $K_2C_4H_4O_6$.**

This salt results from the neutralization of potassium hydrogen-tartrate by potassium carbonate, the reaction being:—

$$2KHC_4H_4O_6 + K_2CO_3 = 2K_2C_4H_4O_6 + CO_2 + H_2O.$$

The addition of calcium carbonate in the preparation of tartaric acid also causes its formation, and if the liquid be filtered, the clear solution upon evaporation yields potassium tartrate in small colourless four or six-sided prismatic crystals.

It dissolves to the amount of 154 parts in 100 parts of water at 60° F., the solution becoming almost solid upon the careful addition of acetic acid. Four parts dissolve in one part of boiling water.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 109.)

POTASSIUM SODIUM TARTRATE (SYNS. *Rochelle Salt. Soda Tartarata. Sodæ Potassio Tartras. Sel de Seignette*). **Formula, $KNaC_4H_4O_6.4H_2O$.**

May be produced by the substitution of sodium carbonate for the potassium carbonate required in the preparation of the salt last described. On evaporation, large crystals of the potassium sodium tartrate are obtained.

The reaction is as follows :—

$$2KHC_4H_4O_6 + Na_2CO_3 = 2KNaC_4H_4O_6 + CO_2 + H_2O.$$

The composition of the crystals is $KNaC_4H_4O_6.4H_2O$, and they are eight-sided right-rhombic prisms, efflorescent in dry air. When heated, they melt in their water of crystallization, but as the temperature increases, the mass boils, and is rendered quite anhydrous at 420° F., the residue, when cold, being a thick, transparent, deliquescent mass, which, when further heated, chars, and leaves a mixture of carbon and potassium sodium carbonate, $KNaCO_3$.

Water dissolves about 66 per cent. of the crystallized salt at 60° F. ; but at 212° F. it takes up five times its weight.

It is used to prevent the precipitation of cupric salts by the addition of potassium hydrate in excess ; a solution thus obtained being employed for the detection and estimation of glucose under the name of *Fehling's solution.*

(*For analysis, see Author's* **Analytical Chemistry**, *page* 109.)

CALCIUM TARTRATE (SYN. *Tartrate of Lime*). **Formula, $CaC_4H_4O_6$.**

Is formed by the addition of calcium chloride to a soluble neutral tartrate. It exists in combination with potassium hydrogen tartrate in *crude argol.* It is also produced by the addition of solution of tartaric acid to calcium hydrate. It dissolves readily in potassium hydrate, potassium hydrogen tartrate, acetic and the stronger acids ; also in ammonium chloride. Unlike calcium citrate, which is more soluble in cold than in boiling water, it is dissolved most readily by the latter. When a solution containing calcium tartrate dissolved in potassium hydrate is boiled, a precipitate separates, which, however, redissolves on cooling.

CUPRIC TARTRATE (SYN. *Tartrate of Copper*). **Formula, $CuC_4H_4O_6$.**

Is an almost insoluble crystalline powder, obtained by adding a neutral solution of a tartrate to cupric sulphate. It is not dissolved by tartaric acid, but is soluble in potassium hydrate and nitric acid. The insolubility of this salt in water has been taken advantage of to separate citric from tartaric acid. The mixed solution, made quite neutral by sodium hydrate, is boiled for some time with a very little ammonium chloride and excess of calcium chloride, and the precipitated calcium citrate and tartrate filtered out. The filtrate is then allowed to stand for twelve hours, once more filtered through the same filter, and the precipitate washed. It is then treated with a little cold potassium

hydrate, which will dissolve the most of the calcium tartrate, and the precipitate again separated by filtration and washed. Afterwards it is digested in a hot solution of *perfectly neutral* cupric chloride, when the whole of the citrate will dissolve, and any insoluble matter will be tartrate.

FERRIC POTASSIUM TARTRATE (SYNS. *Ferrum Tartaratum. Potassio Tartrate of Iron*).

Is produced by the action of potassium hydrogen-tartrate on the ferric hydrate obtained on adding the *liquor ferri persulphatis* to a solution of ammonium hydrate. The product is not thoroughly definite in composition; but the following are probably the reactions involved:—

$$1.\ Fe_23SO_4 + 6NH_4HO = Fe_26HO + 3(NH_4)_2SO_4.$$

$$2.\ 6KHC_4H_4O_6 + Fe_26HO = K_6Fe_26C_4H_4O_6 + 6H_2O.$$

The solution is evaporated and scaled at a temperature not exceeding 100° F. Thus prepared, it is in thin transparent scales of a deep garnet colour, slightly sweetish and astringent in taste, soluble in water, and sparingly soluble in spirit.

When heated to 300° F. it decomposes, evolving water and carbonic anhydride, leaving potassium carbonate, ferric oxide, and charcoal. If in solution, it begins to decompose at about 150° F., a basic ferric salt being deposited. When boiled with potassium hydrate it yields a precipitate of ferric hydrate, leaving potassium tartrate in solution.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 111.)

PLUMBIC TARTRATE (SYN. *Tartrate of Lead*). **Formula, $PbC_4H_4O_6$.**

Is produced by the addition of tartaric acid or a tartrate to a solution of plumbic acetate or nitrate. It is dissolved with ease by nitric and tartaric acids; and when heated in a vessel which is closed whilst hot, it will take fire if poured out upon paper or other inflammable substance after it has cooled, forming a *pyrophorus*.

ANTIMONIOUS and ANTIMONIC TARTRATES. Formulæ, $Sb_23C_4H_4O_6$ *and* **$Sb_25C_4H_4O_6$.**

Are produced by the solution of the corresponding oxide in tartaric acid, and the addition of alcohol, in which they are insoluble.

POTASSIUM ANTIMONYL TARTRATE (SYNS. *Tartar Emetic. Antimonium Tartaratum. Antimonii Potassio Tartras. Stibiated Tartar. Tartre Stibié*). **Formula, $2(KSbOC_4H_4O_6).H_2O$.**

This well-known and valuable salt is the product of the action of **potassium hydrogen-tartrate** upon **antimonious oxide**, the mixture being allowed to stand twenty-four hours for the entire conversion of the oxide to take place. The following represents the reactions which occur:—

$$2KHC_4H_4O_6 + Sb_2O_3 = 2KSbOC_4H_4O_6 + H_2O.$$

Tartar emetic crystallizes in small rhombic octahedrons, which when dissolved in water and treated with a few drops of mineral acid are decomposed, depositing a mixture of potassium hydrogen-tartrate and a basic salt of antimony, soluble in excess of hydrochloric acid. Mixed with an alkaline hydrate,

antimonious oxide is deposited, soluble in excess. Heated on charcoal, a globule of antimony is left, surrounded by an incrustation of oxide.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 110.)

The B.P. gives one molecule of water to one molecule of the salt, thus: $KSbOC_4H_4O_6.H_2O$; but other authorities only allow the same amount of water to two molecules of the *tartar emetic*, and as this has been shown to be correct, it is the best formula to adopt. Cold water dissolves about 7 per cent. of potassium antimonyl tartrate; boiling water taking up 53 per cent.

Its reaction is acid; and the introduction of alcohol causes a immediate precipitation. A solution in sherry, in which it is not very soluble, is the official *vinum antimoniale.*

The previous addition of a small quantity of boiling distilled water would be desirable, and is a practice frequently adopted.

An ointment prepared from tartar emetic is employed in skin diseases.

HYDROGEN CITRATE (SYN. *Citric Acid*). **Formula, $H_3C_6H_5O_7.H_2O$. Molecular Weight, 192.**

May be extracted from lemon juice. It is also contained in oranges and many edible fruits. Unlike tartaric acid, its occurrence as a calcium or potassium acid salt is the exception; the free state being, as a rule, that in which it is found. Thus, it is not necessary to add any calcium chloride in the preparation, which is as follows:—

Lemon juice is heated to boiling, calcium carbonate added until effervescence ceases, and the liquid is filtered whilst hot; the precipitated calcium citrate is washed with hot water, and decomposed by sulphuric acid. The whole is then filtered, to remove the bulk of the calcium sulphate, the filtrate is evaporated to a density of 1·21, when the remainder of calcium sulphate crystallizes out, and the clear solution of citric acid is then crystallized.

The reactions are:—

$$1.\ 2H_3C_6H_5O_7 + 3CaCO_3 = Ca_32C_6H_5O_7 + 3CO_2 + 3H_2O.$$
$$2.\ Ca_32C_6H_5O_7 + 3H_2SO_4 = 2H_3C_6H_5O_7 + 3CaSO_4.$$

Citric acid is usually met with in colourless crystals, of which the right rhombic prism is the primary form; very soluble in water, less soluble in rectified spirit, and insoluble in pure ether. The crystals dissolve in three fourths of their weight of cold, and in half their weight of boiling water. The diluted aqueous solution has an agreeable acid taste. When the solution is made by dissolving thirty-four grains of the acid in one ounce of water, it resembles lemon juice in strength and in the nature of its acid properties, and, like lemon juice, it undergoes decomposition and becomes mouldy by keeping. When heated to redness, it is decomposed, blackens slowly, and then burns entirely away.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 110.)

A solution of citric acid dissolves zinc, magnesium, and iron, with evolution of hydrogen. The acid known as *aconitic* and also *equisetic*, having the formula $H_3C_6H_3O_6$, is the result of subjecting citric acid to dry distillation. It remains in the retort, provided the temperature employed does not much exceed 350° F. The acid is identical with that contained in official and other varieties of aconite, and in several members of the *Equisetaceæ*. It may be purified from undecomposed citric acid and a few bye-products by solution in ether.

Citric acid forms the class of salts known as **citrates**, of which three forms can exist, viz.: *di-hydrogen*, such as $KH_2C_6H_5O_7$; *mon-hydrogen*, such as $BaHC_6H_5O_7$; and *neutral*, such as $K_3C_6H_5O_7$ and $Ba_32C_6H_5O_7$.

(*For detection and separation of Citric Acid and Citrates, see Author's* **Analytical Chemistry**, *page* 78.)

LITHIUM CITRATE (SYN. *Lithiæ Citras*). **Formula, $Li_3C_6H_5O_7$.**

Is the result of the addition of lithium carbonate to citric acid solution until effervescence ceases:—

$$3Li_2CO_3 + 2H_3C_6H_5O_7 = 2Li_3C_6H_5O_7 + 3CO_2 + 3H_2O.$$

The solution thus obtained is evaporated, and the residue dried at a temperature of 240° F. The mass, after cooling and triturating, is a white amorphous powder, deliquescent, and soluble in water without leaving any residue. Heated to redness it blackens, evolving inflammable gases; and the residue, burned at a low red heat with free access of air, leaves a white residue of lithium carbonate.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 110.)

AMMONIUM CITRATE (SYN. *Ammoniæ Citras*). **Formula, $(NH_4)_3C_6H_5O_7$.**

This salt is produced by neutralizing a solution of citric acid with ammonium hydrate; the reaction being:—

$$3NH_4HO + H_3C_6H_5O_7 = (NH_4)_3C_6H_5O_7 + 3H_2O.$$

Is official as a solution,—*liquor ammoniæ citratis*, B.P.,—but it cannot be obtained crystallized, as it decomposes by evaporation; leaving di-ammonium hydrogen citrate $(NH_4)_2HC_6H_5O_7$.

SODIUM CITRATE (SYN. *Sodæ Citras*). **Formula, $Na_3C_6H_5O_7$.**

Crystallizes from a solution of citric acid which has been neutralized by the sodium carbonate, by spontaneous evaporation. The crystals are efflorescent and slightly soluble in alcohol. It is not of pharmaceutical importance; but a solution containing it together with sodium tartrate, results from the action of water upon *sodæ citro-tartras effervescens*, B.P., which is prepared by mixing 17 ounces of sodium hydrogen carbonate with 8 ounces of tartaric and 6 ounces of citric acid, and heating the whole to 220° F. until the powder granulates by stirring.

This is the article commonly sold as "effervescing citrate of magnesia." Frequently, however, the citric acid is omitted, and its place supplied by the much less expensive tartaric acid. The mixture forms better granules if some finely powdered loaf sugar be added, and the best makers also add about 3 per cent. of magnesium sulphate.

POTASSIUM CITRATE (SYN. *Potassæ Citras*). **Formula, $K_3C_6H_5O_7$.**

Is produced by the addition of potassium carbonate to citric acid until a neutral solution results, which is then evaporated, and the residue caused to granulate by stirring after the pellicle forms:—

$$3K_2CO_3 + 2H_3C_6H_5O_7 = 2K_3C_6H_5O_7 + 3CO_2 + 3H_2O.$$

Thus prepared it is a white powder of saline feebly acid taste, deliquescent, and very soluble in water, but insoluble in absolute alcohol. Heated, it chars and finally leaves potassium carbonate.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 110.)

CALCIUM CITRATE (SYN. *Citrate of Lime*). **Formula, $Ca_32C_6H_5O_7$.**

Is precipitated on adding calcium chloride to a neutral citrate, agitating well, and boiling, thus:—

$$2K_3C_6H_5O_7 + 3CaCl_2 = Ca_32C_6H_5O_7 + 6KCl.$$

It is soluble in ammonium chloride and cupric chloride; forming cupric citrate, which is soluble in water; thus differing from cupric tartrate, which is insoluble.

MAGNESIUM CITRATE (SYN. **[True]** *Citrate of Magnesia*). **Formula, $Mg_32C_6H_5O_7$.**

May be formed by the action of heat on a mixture of magnesium oxide or carbonate and citric acid. It is not used in this country, and is too deliquescent to be obtained in definite crystals from a solution; but may be precipitated (from an aqueous solution) as a white powder by means of alcohol, in which it is insoluble. It is a wonderfully tasteless and efficient purgative, and is used in France as the basis of a preparation called *limonade purgative*. It is best produced in solution when required by mixing magnesium carbonate with a little sugar, adding water, and stirring in a solution of an equivalent weight of citric acid. Messrs. Southall, of Birmingham, prepare powders for use on this principle; and the author has received a beautiful sample of true granular effervescent citrate from Messrs. Howard, of Stratford.

In the B.P. *liquor magnesiæ citratis*, magnesium citrate is first prepared in the presence of a good excess of citric acid, and the latter is then utilized to produce carbonic anhydride with the potassium hydrogen-carbonate. If the whole be properly and quickly corked, the pressure of the enclosed gas will be about $1\frac{1}{2}$ atmosphere, and it will consequently effervesce freely on opening the bottle.

CUPRIC CITRATE (SYN. *Citrate of Copper*). **Formula, $Cu_32C_6H_5O_7$.**

This salt, unlike cupric tartrate, is soluble in water. It is formed, together with calcium chloride, when calcium citrate is digested in pure neutral cupric chloride.

(*See Author's* **Analytical Chemistry**, *page* 78.)

FERRIC CITRATE (SYNS. *Ferri Citras. Citrate of Peroxide of Iron*). **Formula, $Fe_22C_6H_5O_7$.**

Results from the solution of freshly precipitated ferric hydrate in a hot solution of citric acid:—

$$Fe_26HO + 2H_3C_6H_5O_7 = Fe_22C_6H_5O_7 + 6H_2O.$$

It cannot be crystallized; but by evaporating and pouring out the syrupy liquid formed, on glass plates, it may be procured in scales. It does not form any precipitate when treated with potassium ferrocyanide. The solution, however, acquires a blue colour, dischargeable by ammonium hydrate. It is contained in the following B.P. salts.

Ferri et Ammoniæ Citras (SYN. *Ferri Ammonio Citras*). **Formula indefinite.**

In the B.P. process for making this scale preparation, ferric hydrate is first made from *liquor ferri persulphatis* by the action of ammonium hydrate.

It should be noticed, that the ferric sulphate is directed to be added to the ammonium hydrate, so as to prevent the precipitate containing an oxy sulphate,

which would materially affect the appearance of the scale. The pure ferric hydrate first made is dissolved in excess of citric acid solution by the aid of heat, and when cold the acidity is neutralized by the addition of a slight excess of ammonium hydrate. The whole is then filtered, evaporated, and scaled at a temperature not exceeding 100° F.

This salt, *ferri et ammonii citras*, is in thin transparent scales of a deep-red colour, slightly sweetish and astringent in taste. It feebly reddens litmus paper, is soluble in water, but almost insoluble in rectified spirit. Heated with solution of potash, it evolves ammonia and deposits ferric hydrate. When incinerated with exposure to air, it leaves not less than 27 per cent. of ferric oxide, which is not alkaline in reaction, because this scale differs from *ferrum tartaratum* in containing no potassium.

A solution of 160 grains in a pint of sherry constitutes *vinum ferri citratis*, B.P.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 111.)

Ferri et Quiniæ Citras (Syn. *Citrate of Iron and Quinine*). **Formula indefinite.**

This valuable salt contains three citrates, viz.: those of iron, quinine, and ammonium.

The B.P. process is divided into five distinct stages:—

1. Precipitation of ferric hydrate from ferric sulphate by pouring it into ammonium hydrate.

2. Precipitation of pure *quinia* from *quiniæ sulphas*, previously dissolved in dilute sulphuric acid, by ammonium hydrate.

3. Solution (after washing) of both these precipitates in excess of citric acid solution.

4. The addition of ammonium hydrate, carefully avoiding excess, so as to leave the solution feebly acid.

5. Evaporating and scaling at 100° F.

Characters and Tests.—Thin scales of a greenish golden-yellow colour, somewhat deliquescent, and entirely soluble in cold water. The solution is very slightly acid, and is precipitated by sodium hydrate, and by both ferro- and ferri- cyanides. The addition of a little ammonium hydrate causes a precipitate of hydrated *quinia*, soluble in a free excess.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 112.)

The fact that the solution affects both potassium ferro- and ferri- cyanides, and the greenish colour of the scales, prove that the iron is partly reduced in this preparation to the ferrous state, which is not the case in the other scale preparations already mentioned. This is owing to the fact that the amount of ammonium hydrate which is added is not sufficient to fully saturate the acid, otherwise quinia would be precipitated. The colour of the scales can be altered at will, according to the quantity of ammonium hydrate used.

BISMUTHOUS CITRATE (Syn. *Citrate of Bismuth*). **Formula,** $BiC_6H_5O_7$.

Is the white precipitate formed on adding a neutral citrate to a solution of bismuthous nitrate (or chloride). It is soluble in ammonium salts, and a solution in ammonium citrate and nitrate constitutes *liquor bismuthi et ammoniæ citratis*, B.P., which is prepared by distinct steps as follows:—

1. Bismuthous nitrate is prepared by dissolving bismuth in nitric acid, and evaporating to expel any excess of nitric acid.

2. To this solution citric acid is added, and then ammonium hydrate carefully until the precipitate first formed is redissolved.

By this means a colourless neutral or only feebly alkaline solution is obtained, *which will mix with any quantity of water without forming a precipitate.* It has a specific gravity of 1·122, and contains an amount of bismuth representing 3 grains of Bi_2O_3 per fluid drachm.

(*For analysis, see Author's* **Analytical Chemistry**, *page* 111.)

VII. AROMATIC ACIDS.

HYDROGEN BENZOATE (SYNS. **Benzoic Acid.** *Benzoyl Hydrate. Flowers of Benzoin*). **Formula, $HC_7H_5O_2$.**

This acid occurs in several official substances, viz., *balsamum Peruvianum, balsamum tolutanum, styrax,* and *benzoinum.* It is frequently prepared by heating the last-named body in an iron vessel, having inverted over it a conical cap of thick paper, and covering this by a filtering septum of strong unsized paper. The whole is then subjected to a gradually increasing heat for a time varying with the amount of gum resin used. A small quantity will cease to evolve the acid in an hour or less, whilst several pounds will take five hours or more. The covering of filter paper is requisite to absorb oily and other bye products, and to render it impossible for the sublimate to fall back into the vessel containing the benzoin. By breaking the residual mass into small fragments and re-heating, the total amount may approximate to 12 or 13 per cent. The residue of the first operation can be more readily broken, and is less liable to be charred, if the powdered benzoin be mixed with fragments of pumice or sand. In the wet process, benzoic acid may be extracted by digesting 10 parts of benzoin with 6 parts of calcium hydrate and 100 parts of water for five or six hours, boiling for half an hour, filtering, and well washing the residue. The solution is then evaporated to half the bulk, and rendered decidedly acid by hydrochloric acid, upon which the calcium benzoate contained in the solution is decomposed, and the benzoic acid is deposited in white crystalline scales on the solution becoming cold. The impurities still contained may be removed by subjecting it, after drying, to sublimation, or by solution in boiling water and recrystallization. The vanilla like odour of pharmaceutical benzoic acid is owing to a trace of a volatile oil formed during sublimation, and possessing the medicinal properties for which the acid is valuable. Thus the product of the wet process requires to be sublimed before it acquires the whole of its Pharmacopœia qualities.

Benzoic Acid should be in light feathery crystalline plates and needles, which are flexible, nearly colourless, and have an agreeable aromatic odour, resembling that of benzoin. It is sparingly soluble in water, but is readily dissolved in rectified spirit, soluble also in solutions of the caustic alkalies and of lime; and it is precipitated from these on the addition of hydrochloric acid unless the solution be very dilute. It melts at 248°, and boils at 462° F. When heated to the last named temperature, it passes off in vapour, leaving only a slight residue.

The reactions taking place in the wet preparations are:—

$$1.\quad 2HC_7H_5O_2 + Ca2HO = Ca2C_7H_5O_2 + 2H_2O.$$

$$2.\quad Ca2C_7H_5O_2 + 2HCl = 2HC_7H_5O_2 + CaCl_2.$$

The oxidizing action of the air on benzoyl aldehyd also produces this acid by the simple addition of one atom of oxygen. A process of great practical interest and importance consists in the formation of naphthalic (also called *phthalic*) acid by oxidizing naphthalin with nitric acid, and the transformation of this by neutralization with calcium hydrate, and subsequent heating with

excess of the latter. The calcium phthalate must be obtained in a dry state, and then afterwards calcined with the hydrate at 630° to 660° F. for six or seven hours. On treating the cooled product with boiling water, filtering, and adding hydrochloric acid in excess, benzoic acid crystallizes out as the temperature becomes lower. The following represents the decompositions which are known to take place:—

1. $C_{10}H_8 + 6HNO_3 = H_2C_8H_4O_4 + H_2C_2O_4 + 4NO + N_2O_3 + 3H_2O$.
(Naphthalin.) (Phthalic Acid.)
2. $H_2C_8H_4O_4 + Ca2HO = CaC_8H_4O_4 + 2H_2O$.
(Calcium Phthalate.)
3. $2CaC_8H_4O_4 + Ca2HO = Ca2C_7H_5O_2 + 2CaCO_3$.
(Calcium Benzoate.)

The reaction by which benzoic acid is derived from calcium benzoate has already been given. A characteristic quality of benzoic acid, distinguishing it from cinnamic acid, is its resistance to oxidation by dilute nitric and chromic acids, which yield with the latter benzoic aldehyd.

Benzoates of the monad metals, when heated, yield benzoyl aldehyd; if mixed with an alkaline formate alone, they leave a carbonate (except the ammonium and argentic salts) giving off benzene and other hydrocarbons. Heated in contact with the air, all benzoates produce the metal, its oxide, or its carbonate, evolving carbonic anhydride and water.

(*For detection of Benzoic Acid and Benzoates, see Author's* **Analytical Chemistry**, *page* 79.)

AMMONIUM BENZOATE (SYN. *Ammoniæ Benzoas*). **Formula, $NH_4C_7H_5O_2$.**

Is the result of acting upon benzoic acid with ammonium hydrate:—

$$NH_4HO + HC_7H_5O_2 = NH_4C_7H_5O_2 + H_2O.$$

During evaporation this salt decomposes, evolving ammonia gas, and leaving a compound in which the freed acid is united to the neutral compound under consideration. It is a deliquescent salt, in colourless laminar crystals, soluble in water and in alcohol. It is entirely volatile by heat, and a strong aqueous solution, when acidulated with a mineral acid, lets fall crystals of benzoic acid.

POTASSIUM BENZOATE. Formula, $KC_7H_5O_2$.

Is formed by acting on an aqueous solution of benzoic acid with potassium carbonate. If an alcoholic solution of benzoic acid be employed, no decomposition occurs; on the contrary, a solution of potassium benzoate is decomposed by passing carbonic anhydride through it, benzoic acid remaining in solution.

CALCIUM BENZOATE (SYNS. *Calcic Benzoate. Benzoate of Lime*). **Formula, $Ca2C_7H_5O_2$.**

Is contained in the solution produced on boiling benzoin (gum resin) with calcium hydrate. It dissolves in water to the extent of about 3½ per cent., if it be cold; to a much greater amount, if warm.

FERRIC BENZOATE (SYNS. *Benzoate of Iron. Benzoate of Peroxide of Iron*). **Formula, $Fe_26C_7H_5O_2$.**

Is soluble in water, and may be obtained in yellow crystals by dissolving ferric hydrate in a watery solution of benzoic acid, and evaporating. When redissolved it decomposes, depositing an oxy-salt or hydrate-salt. Alcohol causes the same alteration. *Ferrous Benzoate* is dissolved by water.

HYDROGEN CINNAMATE (Syn. **Cinnamic Acid**). **Formula, $HC_9H_7O_2$.**

This acid may be obtained from cinnyl alcohol and cinnamyl hydride by oxidation.

By acting on styracin (mentioned under **Cinnyl Hydrate**) with potassium hydrate in a strong boiling solution, cinnamic acid and the alcohol whence it is derived are simultaneously formed. The most economical processes are—

1. To extract it from the crystalline matter found coating the interior of the leaden vessels in which oil of cinnamon is brought to this country.

2. To act on balsam of Peru with calcium hydrate made into a thick paste with water.

I. This crystalline deposit is treated with boiling rectified spirit, and filtered; the impure cinnamic acid, which separates on cooling, dissolved in sodium carbonate and pure water, hydrochloric acid added, and the crystals, which fall on cooling, pressed and dried. The portion insoluble in hot spirit is plumbic cinnamate. If it be boiled with sodium carbonate, and filtered, the filtrate on acidulation deposits the acid.

II. If the mixture above mentioned be boiled and filtered, the residue again boiled (several times) with water, and the united filtrates mixed, calcium cinnamate separates in a tolerably pure state as the temperature becomes low. By decomposing this with hydrochloric acid and hot water, crystals may be procured after some time. On subjecting these to solution in ammonium hydrate and reprecipitation, or to sublimation, the pure acid results.

Cinnamic acid is only slightly soluble in water at 60° F., but freely in hot water. A valuable distinction from benzoic acid consists in the fact that by distillation with plumbic dioxide, benzoyl hydride (recognised by its odour) is evolved. The same reaction occurs with sulphuric acid and potassium dichromate.

The precipitate, on introducing a neutral cinnamate into a ferric solution, is yellow. Benzoates produce a more or less red deposit. Manganous benzoate is soluble. Manganous cinnamate, after a little time, is yellow, crystalline, and insoluble. The cinnamates are of too slight importance to be given in a work of this character. One only is an exception.

CINNYL CINNAMATE. **Formula, $C_9H_9C_9H_7O_2$.**

It occurs in *styrax præparatus*, B.P., in the form of styracin, which is its usual name.

It is an oily liquid obtained by expression from the impure substances used in making cinnyl hydrate (*vide ante*). By other methods of preparation it is procured in prismatic crystalline masses, easily dissolved by ether.

HYDROGEN SALICYLATE (Syns. **Salicylic Acid.** *Oxybenzoic Acid*). **Formula, $C_7H_6O_3$, or $H_2C_7H_4O_3$.**

Was originally produced by the oxidation of salicylic aldehyd (oil of meadow-sweet), but is now extensively prepared from sodium phenate, made by heating carbolic acid with potassium hydrate:—

$$C_6H_5HO + NaHO = C_6H_5NaO + H_2O.$$

The salt thus formed is then heated gradually from 212° up to 500° in a retort through which a stream of carbonic anhydride is kept passing. During this process a little carbolic acid is re-formed, and distils over, while sodium salicylate remains in the retort:—

$$2C_6H_5NaO + CO_2 = Na_2C_7H_4O_3 + C_6H_5.HO.$$

The sodium salicylate is then dissolved in a small quantity of water, an composed by hydrochloric acid, which the salicylic acid precipitates in matic crystals. It is freely soluble in alcohol, ether, and hot water, but to the extent of one part in 1800 of cold water. Heated, it melts and de poses, giving off carbolic acid. It is a powerful antiseptic, being used sively to preserve milk and beer, and its sodium salt, which is very solu water, has a great reputation in the treatment of acute rheumatism.

Its ferric salts are soluble in water, and have a beautiful violet colour.

(*For detection of Salicylic Acid, see Author's* **Analytical Chemistry**, *page* 80.)

HYDROGEN GALLATE (SYN. **Gallic Acid**). **Formula, $H_3C_7H_3O_5$.**

Is produced by the decomposition of tannin (*acidum tannicum*, B.P. boiling with dilute acids. The B.P. method is to expose powdered moistened with water, to atmospheric action. The temperature must b to 80° F., the moist state should be maintained for about six weeks termination of that period the galls are boiled with three parts of water, fi and the acid which falls on cooling dried slightly by exposure to th The adherent water is removed by pressure between filtering paper, an product, unless nearly white in colour, redissolved in hot water, decolo by animal charcoal, and crystallized.

Characters and Tests.—Crystallizes in acicular prisms or silky needles, times nearly white, but generally of a pale fawn colour. It requires abo parts of cold water for its solution, but dissolves in three parts of boiling Soluble also in rectified spirit. The crystalline acid, when dried at 212°, 9.5 per cent. of its weight. It leaves no residue when burned with free of air.

When heated, it loses water, becoming converted into pyrogallic A solution of gallic acid in glycerin, containing one part in six by weig the acid, is termed in the B.P. *glycerinum acidi gallici*. A moderate d of heat should be applied to effect perfect solution. It possesses a sl acid astringent taste. Ethereal and alcoholic solutions also redden paper.

Gallic Acid differs from *tannic acid* also by not reacting with albume alkaloid salts. The acid salts of this acid are alone undecomposed by sure to the air.

Solid gallic acid forms a bright-red liquid with potassium and a nium hydrates. Strong sulphuric acid gives, when hot, a similar reaction the solution thus formed lets fall a red precipitate on the addition of The weak solution of calcium hydrate known as *lime water*, when added little gallic acid solution, forms a white precipitate, changing through blue violet to a purplish colour.

Potassium permanganate may be employed to estimate this acid, by a tion of known strength (say 1–10 equivalent in a litre, or 1·58 per cent.) run into a solution of a weighed quantity of the gallic acid to be estim until it acquires a faint pink tinge.

When gallic acid is added to auric and argentic salts, the metal is libe slowly at the ordinary temperature; and this reduction affords valuable m of obtaining desirable results in photography. On submitting the mixtu heat, very rapid deposition of the metals occurs.

Gallic acid has been discovered to be a tetrad within the last few yea compound having the composition $Ba_2C_7H_2O_5$ having been made.

The gallates may be of at least six classes; viz., mon-, di-, tri-, and metallic, acid, and basic salts.

(*For detection of Gallic Acid, see Author's* **Analytical Chemistry**, *page* 81.)

Ferric Gallate.—Indefinite in composition, and of a blue colour, producing a colourless ferrous salt on boiling, carbonic anhydride being evolved.

Veratria Gallate.—Is the natural form in which veratria exists in the following official vegetable productions,—*sabadilla*, *veratri viridis radix*, *colchici cormus*, and *colchici semina*.

In preparing veratria, precipitation by ammonium hydrate is adopted, in order to remove the gallic acid in combination with that alkaloid, the ammonium hydrate being converted into ammonium gallate.

TANNIN (SYN. *Tannic Acid*). **Formula, $C_{27}H_{22}O_{17}$. Molecular Weight, 618.**

Is usually considered to be a glucoside, but as it has been stated to be really an anhydride of gallic acid, we will look at it in this aspect for the time being. Of *tannins* there are many varieties, differing from each other sometimes by chemical and at others by physical peculiarities.

The principal classes chemically distinguished are those forming (like galls, or ordinary tannic acid) blackish or purplish-black precipitates with ferric salts, and those yielding a greenish-brown. The Pharmacopœia tannic acid is recognised by producing a gelatinous precipitate with potassium antimonyl tartrate, and also (when in watery solutions) with sulphuric, hydrochloric, and nitric acids; by giving a purplish black upon adding a ferric solution; by throwing down a greyish compound when a solution of gelatin is introduced into its aqueous solution, and by rendering alkaloids insoluble in water, though soluble in acetic and stronger acids.

To prepare tannic acid, expose powdered galls to a damp atmosphere for two or three days, and afterwards add sufficient ether to form a soft paste. Let this stand in a well-closed vessel for twenty-four hours, then, having quickly enveloped it in a linen cloth, submit it to strong pressure in a suitable press, so as to separate the liquid portion. Reduce the pressed cake to powder, mix it with sufficient ether, to which one sixteenth of its bulk of water has been added, to form again a soft paste, and press this as before. Mix the expressed liquids, and expose the mixture to spontaneous evaporation until, by the aid subsequently of a little heat, it has acquired the consistence of a soft extract, then place it on earthen plates or dishes, and dry it in a hot-air chamber at a temperature not exceeding 212° F.

Thus made, it is found in pale yellow vesicular masses, or thin glistening scales, with a strongly astringent taste and an acid reaction; readily soluble in water and rectified spirit, very sparingly soluble in ether. It leaves no residue when burned with free access of air.

The majority of the forms of tannic acid exhibit an acid reaction (never very decided) towards litmus paper, are astringent but not sharp in taste, and form with gelatin the insoluble compound known as *artificial leather*. They also give the characteristic reactions with ferric salts already mentioned, and show a similar behaviour towards albumen as towards gelatin. Quino-tannic acid (contained in cinchona bark), and the tannin accompanying salicin in willows, as well as that found in catechu, rhatany root, and rhubarb, are of the variety which engenders an insoluble ferric salt of a green colour. The purplish-black ferric salt is produced by the reaction with querco-tannic acids (of the oak), the tannin of bearberry leaves, and that obtained from other sources.

From aqueous solutions the official or gallo-tannic acid is thrown down by sodium and ammonium chlorides, potassium sulphate and acetate, etc.; also by hydrochloric and sulphuric acids.

The phenomenon of the precipitation without alteration of a substance not very soluble in water by one much more so, is by no means uncommon, especially with hydro carbonaceous compounds.

Gallo-tannic acid is taken up with tolerable freedom by both expressed and essential oils. The member of the latter in which it is especially and pre-eminently soluble is oil of bitter almonds. It dissolves also in glyceryl hydrate to the extent of about 15 per cent. (For details of the preparation of the solution see **Glyceryl Hydrate.**) Its solution in glyceryl is official under the name of *glycerinum acidi tannici.* The formation of *cupric tannate,* —$Cu_3(C_{27}H_{22}O_{17})_2$ (?),—when a solution of cupric acetate is added to a watery solution of tannic acid, may occasionally prove serviceable as a test. It is of a pinkish colour.

(*For detection of Tannic Acid, see Author's* **Analytical Chemistry**, *page* 81.)

HYDROGEN PYROGALLATE (SYNS. **Pyrogallic Acid.** *Dioxyphenic Acid*). **Formula, $H_3C_6H_3O_3$.**

When gallic acid, or a watery extract of galls, is heated in an iron vessel covered with a diaphragm of filter paper, and having a thick paper cap inverted over it, this acid sublimes in almost white, very light crystalline flocks. The heat employed must last for nearly twelve hours, and not vary much below 356° or above 365° F. The most advantageous method is to sublime gallic acid mixed with fragments of pumice stone, in a vessel through which a stream of carbonic anhydride may be passed. The crystals, when accurately examined, are seen to be prismatic plates. At 60° F. pyrogallic acid dissolves in rather more than twice its weight of water, is more soluble in hot water, but less so in ether and alcohol. It is derived from gallic acid by the withdrawal of carbonic anhydride, thus:—

$$H_3C_7H_3O_5 = H_3C_6H_3O_3 + CO_2.$$

It is employed as a reducing agent by photographers, and is also in commercial demand for making hair dyes. When in solution it is decomposed by exposure to the air, becoming brown by oxidation. In consequence of very small quantities of nitrous acid turning it brown, a colourless, watery solution may be employed as a test for that body. It is a weak acid, not decomposing all carbonates. The most important of the pyrogallates will be found undermentioned. The only noticeable general reactions are their propensity to become coloured by atmospheric action, and the reducing action they exert upon auric, platinic, argentic, and mercuric salts.

(*For detection of Pyrogallic Acid, see Author's* **Analytical Chemistry**, *page* 81.)

Ammonium Pyrogallate is formed when ammonium hydrate is added to the acid. It is employed as a test, becoming brown by the influence of the air.

Potassium Pyrogallate is the salt, the formation of which determines the absorption of oxygen in gas analysis. (*See* **Nitrogen.**) It becomes first purplish, afterwards dark-brown or black, by combination with oxygen.

Argentic Pyrgoallate does not exist; pyrogallic acid causing the deposition of the metal from argentic salts.

Calcium Pyrogallate forms the fine reddish solution, quickly becoming deep brown, resulting from the addition of calcium.

Ferrous Pyrogallate is contained in the beautiful blue solution produced by introducing a ferrous salt into aqueous pyrogallic acid. A slight contamination with a ferric salt secures the formation of a green-coloured liquid.

Ferric Pyrogallate is a constituent of the fine red solution, the formation of which occurs on introducing a dissolved ferric salt into pyrogallic acid solution.

CHAPTER XVII.

ETHERS.

THE salts formed by the unsaturated hydrocarbons acting as basylous radicals, are called ethers.

They are of three classes, viz.: haloid, simple, and compound.

I. HALOID ETHERS.

Are the result of the displacement of one or more atoms of hydrogen from a saturated hydrocarbon, by Cl, Br, or I, and are therefore the chlorides, bromides, or iodides of the basylous radical corresponding. They may also be viewed as the result of the displacement of HO from an alcohol by Cl, Br, or I; and, like the alcohols, they run in series, and are monatomic, diatomic, or triatomic.

(*a*) Monatomic Haloid Ethers of the Series $C_nH_{2n-1}X$.

These may be produced by the following general methods :—

1. By the direct action of chlorine or bromine upon the corresponding saturated hydrocarbon :—

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl.$$

2. By passing dry hydrochloric acid gas into the alcohol and then distilling:—

$$C_2H_5HO + HCl = C_2H_5Cl + H_2O.$$

3. By heating the alcohol with bromine and iodine and phosphorus, so forming phosphorous bromide or iodide, which then react, thus :—

$$3C_2H_5HO + PBr_3 = 3C_2H_5Br + H_3PO_3.$$

$$3C_2H_5HO + PI_3 = 3C_2H_5I + H_3PO_3.$$

The haloid ethers are especially useful in making other compounds, owing to the variety of decompositions they undergo, of which the following are worthy of special note :—

1. The haloid ether, treated with potassium hydrate (or better, with moist argentic oxide), forms the corresponding alcohol :—

$$2C_2H_5I + Ag_2O + H_2O = 2C_2H_5HO + 2AgI.$$

2. The haloid ether, acted on by a potassium or sodium alcoholate, yields the simple ether corresponding. Thus :—

$$C_2H_5I + Na(C_2H_5)'O = (C_2H_5)_2O + NaI.$$

3. By double decomposition with the silver salt of the required acid, any compound ether may be obtained from the haloid ether. Thus :—

$$C_2H_5I + AgC_2H_3O_2 = C_2H_5.C_2H_3O_2 + AgI.$$

4. By acting on the haloid ether with nascent hydrogen, we can obtain the original **paraffin** :—

$$C_2H_5I + H_2 = C_2H_6 + HI.$$

5. By heating the haloid ether in a sealed tube with alcoholic ammonia, we obtain the bromide or iodide of the corresponding **amine**. (*See* **Amines**.)

6. Acted upon by potassium cyanide, haloid ethers yield the cyanide of their basylous radical; thus, methyl iodide and potassium cyanide give methyl cyanide :—

$$CH_3I + KCN = CH_3CN + KI.$$

But, as already seen (*page* 177), the **cyanides** of monad organic radicals are also the **nitrils** of the triad basylous radicals immediately higher in carbon value; therefore the above reaction may be shown as forming ethenyl or aceto-nitril, thus :—

$$CH_3I + KCN = (C_2H_3)'''N''' + KI.$$

It will be sufficient to glance at the haloid ethers of methyl, those of ethyl, propyl, butyl, and amyl being very similar, only having higher boiling points as the number of their carbon atoms increases.

METHYL CHLORIDE (SYN. *Chloromethane*). **Formula, CH_3Cl.**

May be prepared by distilling together sodium chloride, sulphuric acid, and wood spirit :—

$$CH_3HO + H_2SO_4 = CH_3HSO_4 + H_2O.$$
$$CH_3HSO_4 + NaCl = CH_3Cl + NaHSO_4.$$

It is a gas with a peculiarly sweetish odour and taste, and only slightly soluble in water. It is, like most ethereal chlorides, combustible, and burns with a greenish flame. It is now prepared on an industrial scale from the residues obtained in the manufacture of sugar from beetroot. Exposed to sunlight in contact with excess of chlorine, it first becomes methene chloride, then chloroform, and finally carbon tetrachloride.

METHYL IODIDE (SYN. *Iodomethane*). **Formula, CH_3I.**

Is prepared by the action of phosphorus and iodine upon methyl hydrate (wood spirit), phosphoric acid being at the same time formed :—

$$P_2 + 5I_2 + 10CH_3HO = 10CH_3I + 2H_3PO_4 + 2H_2O.$$

It is a slightly combustible, colourless, volatile liquid, evolving violet vapours (iodine) when inflamed. It owes its interest to its employment in the preparation of the radical methyl in the free state, by heating in a sealed tube with zinc and water :—

$$2CH_3I + Zn = ZnI_2 + (CH_3)_2.$$

METHYL BROMIDE (SYN. *Bromomethane*). **Formula, CH_3Br.**

Prepared exactly like the iodide, but using bromine instead of iodine. Resembles the iodide closely.

(*b*) Diatomic Haloid Ethers, Series $C_nH_{2n}X_2$.

These bodies are formed :—

1. By the direct action of chlorine on the olefines.
2. By the action of phosphoric bromide or iodide upon the aldehyd

or ketone of the monad series corresponding in number of carbon atoms. Examples :—

$$\underset{\text{(Aldehyd.)}}{C_2H_4O} + PCl_5 = \underset{\text{(Ethene chloride.)}}{C_2H_4.Cl_2} + POCl_3.$$

$$\underset{\text{(Acetone.)}}{C_3H_6O} + PCl_5 = \underset{\text{(Propene chloride.)}}{C_3H_6.Cl_2} + POCl_3.$$

METHENE CHLORIDE (SYNS. *Methylene Chloride. Dichloromethane*). **Formula, CH_2Cl_2.**

According to Perkin, this body is best obtained by agitating an alcoholic solution of chloroform with powdered metallic zinc and a small quantity of ammonium hydrate. The reaction is doubtless brought about by nascent hydrogen, and is accompanied by the formation of marsh gas :—

$$2CHCl_3 + 4H_2 = CH_2Cl_2 + CH_4 + 4HCl.$$

It is a colourless liquid, boiling at 106° F., and not solidifying at 0° F. It has been used as an anæsthetic under the name of *bichloride of methylene.*

ETHENE CHLORIDE (SYNS. *Ethylene Chloride. Dutch Liquid*). **Formula, $C_2H_4Cl_2$.**

Is produced by causing olefiant gas and chlorine to mix together over water, when a yellowish oily liquid forms and sinks to the bottom in drops. It possesses a peculiarly fragrant odour, and burns with a greenish flame. It is interesting as being one of the early discoveries in this branch of chemistry, having been first produced by four Dutch chemists in 1795.

(*c*) Triatomic Haloid Ethers, Series $C_nH_{2n-1}X_3$.

METHENYL CHLORIDE (SYNS. *Chloroform. Formyl Chloride*). **Formula, $CHCl_3$.**

Is prepared by distilling spirit of wine with chlorinated lime and slaked lime in the presence of a considerable quantity of water, when chloroform and calcium formate are produced. This may be represented in one equation as follows :—

$$4C_2H_5HO + 8Ca2ClO = 2CHCl_3 + 3Ca2CHO_2 + 5CaCl_2 + 8H_2O.$$

The real reactions which occur are more probably as follows. Keeping in mind that "chlorinated lime" can exercise both an oxidizing and a chloridizing influence, we may consider that by the former the alcohol is reduced to aldehyd, and that by the latter hydrogen is displaced, forming trichloraldehyd, or chloral :—

$$2C_2H_5HO + 6Cl_2 + O_2 = 2C_2HCl_3O + 6HCl + 2H_2O.$$

Immediately on its formation, however, the chloral is attacked by the calcium hydrate, and decomposed to chloroform and calcium formate :—

$$2C_2HCl_3O + Ca2HO = 2CHCl_3 + Ca2CHO_2.$$

In practice, the ingredients should be mixed and heated gradually, taking care to withdraw the heat the moment the distillation really commences. After the distillation, the crude product is first washed by shaking up with distilled water, and afterwards purified by agitation with an equal bulk of strong sulphuric acid. Finally, the chloroform is separated by a pipette, and rectified over a mixture of calcium chloride and slaked lime. Thus prepared, it is a limpid colourless liquid, of an agreeable ethereal odour, and sweet taste.

Chloroform dissolves in alcohol and ether in all proportions; and slightly in water, communicating to it a sweetish taste. Burns, though not readily, with a green and smoky flame. Specific gravity, 1·49. It is not coloured by agitation with sulphuric acid; leaves no residue and no unpleasant odour after evaporation. It is only very slightly soluble in water (1 in 200).

Besides the well-known anæsthetic properties of its vapour, chloroform is very useful to the analyst as a solvent for alkaloids as well as for iodine, bromine, camphor, resinous bodies, and volatile oils. Its striking power of dissolving alkaloids is utilized in isolating them for toxicological investigations, and in the assay of barks; while its ability to dissolve, and show a colour with minute traces of iodine and bromine is made use of in the detection of these elements. It can be brought into contact with acids and alkalies in watery solution without change, and it is miscible with both turpentine and carbon disulphide. The most common adulterants of chloroform are alcohol, wood-spirit, methylated chloroform, and traces of sulphuric acid. The best reagent for detecting alcohol is a salt obtained by acting on ferric chloride with a mixture of potassium nitrate and ammonium sulphide, and called *ferrous di-nitro sulphide.* If chloroform be shaken up with this substance, it acquires a green colour in presence of the impurities mentioned. A very simple way of detecting alcohol, and at the same time of roughly estimating its amount, is to fill a burette with chloroform up to 20 c.c., and then add water to 100 c.c., shaking violently. Pure chloroform will sink to the bottom in clear globules; but in the presence of alcohol, the liquid, and the surface of the drops, will become dim and opalescent. After the chloroform has settled, a diminution will be observed equal to the amount of alcohol which has been extracted by the water, always allowing for $\frac{1}{10}$ of a c.c., which would be the natural loss by solubility, even with a pure article. Chloroform will keep well in a dark place; but when exposed to air and strong sunlight it will resolve itself into hydrochloric acid, chlorine, and other products, unless it be entirely free from nitryl compounds, in which case it is said not to be affected by light and air. The presence of an exceedingly small quantity of nitric acid in the sulphuric acid used in the purification of chloroform, is sufficient to give it this tendency to spontaneous decomposition. Methylated chloroform can be detected by the offensive smell which it leaves upon a cloth dipped in it, and allowed to dry spontaneously. This smell is owing to its containing about 6 per cent. of an empyreumatic oil, a constituent of which is chlorine, and which is blackened by sulphuric acid. Lately it has been stated that chloroform can be made from methylated spirit so as to be quite undetectable. A good test for small quantities of chloroform is to heat with a little aniline and alcoholic sodium hydrate, when a violent action ensues, and the characteristic smell of an alcoholic cyanide (isonitril) is evolved.

METHENYL BROMIDE (SYN. *Bromoform*). **Formula, $CHBr_3$.**

When potassium hydrate and bromine are caused to act upon alcohol or wood spirit, this substance is formed. It is a heavy liquid, having a specific gravity of 2·13, and is a result of the action of calcium hydrate on bromal, in the same manner that chloroform is a product of the treatment of chloral with that reagent. It imparts its taste, which is sweet, and its smell, which is agreeable, to water, in which, like chloroform, it is slightly soluble.

It dissolves iodine to a large extent, phosphorus and sulphur less rapidly, while it is itself dissolved by the volatile oils, ether, and alcohol.

It decomposes on being boiled with potassium hydrate, potassium bromide and bromate being formed.

It is only slightly combustible.

METHENYL IODIDE (Syn *Iodoform*). **Formula, CHI_3.**

This body may be prepared by mixing solution of potassium hydrate and of iodine in alcohol until a light yellow solution is formed. The excess of alcohol is removed from this by evaporation.

Iodoform melts at 240° to 250° F., and on volatilizing is partially decomposed. It forms greenish-yellow plates, possessing a saffron odour. When mixed with water, it distils without alteration. Acid water and alkaline hydrates do not dissolve it, although it is soluble in all oils, ether, and alcohol. By the action of bromine, bromoform is produced; and by heating in a closed vessel to 300° F. *methylene di-iodide* results. By distillation with mercuric chloride it has been stated to yield *chloroform*, and with mercuric cyanide, *iodocyanoform*.

A trace of alcohol in any liquid is said to be readily determined by a test depending on the formation of iodoform. If the suspected solution be warmed to 150° F., with a little iodine and sodium hydrate, the reaction of these upon the alcohol causes the deposit of a yellowish crystalline body of CHI_3. Many gummy matters, sugars, and hydrates of hydrocarbons, form the same precipitate under similar circumstances, and the potassium iodide and formate simultaneously formed are dissolved out by water, in which the iodoform is insoluble. The simplest explanation of the reaction is:—

$$C_2H_5HO + 6KHO + 4I_2 = CHI_3 + 5KI + KCHO_2 + 5H_2O.$$

It may also be produced by treating alcohol, mixed with twice its weight of crystallized sodium carbonate, dissolved in ten parts of water, with its own weight of iodine. The mixture having been heated to 140° or 180° F. the precipitated iodoform is separated by filtration. More alcohol and sodium carbonate being added, and chlorine passed through, the sodium iodide formed is decomposed by the chlorine, and iodine is set free. A great excess of iodine will altogether prevent the required result.

II. SIMPLE ETHERS.

Are the oxides of the unsaturated basylous hydrocarbon radicals. The only series which directly interests us is the fatty series, the simple ethers of which may be prepared,—

1. By heating sulphuric acid with a continually maintained excess of the alcohol. (*See* **Ethyl Oxide**.)

2. By heating a haloid ether with the potassium or sodium compound of the alcohol. Example: ordinary alcohol, treated with metallic sodium, forms sodium ethylate, and that acted upon by ethyl iodide, yields ethyl oxide. Thus:—

$$2C_2H_5HO + Na_2 = 2C_2H_5NaO + H_2.$$
$$C_2H_5NaO + C_2H_5I = (C_2H_5)_2O + NaI.$$

Besides the ordinary oxide, we can have ethers in which the oxygen is combined with one molecule each of two different radicals, instead of two molecules of the same radical, thus producing a compound intermediate in its boiling point and general properties. For instance, taking the lower end of the series, we find:—

Methyl oxide . .	$(CH_3)_2O$	boiling at	5·8° F.
Methyl ethyl oxide .	$CH_3.C_2H_5.O$	„ „	52·0°
Ethyl oxide . .	$(C_2H_5)_2O$	„ „	96·0°

METHYL OXIDE (SYN. *Methylic Ether*). **Formula, $(CH_3)_2O$.**

Is prepared by heating sulphuric or boracic acids with a continually maintained excess of methyl alcohol.

It is a colourless gas, of ethereal odour and burning with a pale blue flame. It is soluble in cold water, and condenses to a liquid at 5° F. It is by means of this compound that we are enabled to detect ethyl in methyl alcohol. Pure methyl hydrate thus etherified and the vapour passed through a receiver kept at 32° F. by ice, should yield us no liquid ether; but if it contain ordinary alcohol, then ordinary ether will condense.

ETHYL OXIDE (SYNS. *Ether. Ethyl Ethylate. Sulphuric Ether. Æther Purus*). **Formula, $(C_2H_5)_2O$. Molecular Weight, 74. Specific Gravity, ·72. Vapour Density,** *referred to Air*, **2·586.** *Referred to Hydrogen*, **37.**

Is prepared by heating a mixture of rectified spirit of wine and sulphuric acid to a temperature of 284° F., and causing a continuous stream of alcohol to flow into the retort. The reaction is produced in two steps:—

1. The alcohol and sulphuric acid form **ethyl hydrogen-sulphate and water:**

$$C_2H_5HO + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

2. The **ethyl hydrogen-sulphate**, meeting with a fresh quantity of alcohol, forms **ethyl oxide**, and reproduces sulphuric acid, which can then etherify a fresh quantity of alcohol:—

$$C_2H_5HSO_4 + C_2H_5HO = (C_2H_5)_2O + H_2SO_4.$$

Great care must be taken in regulating the temperature and keeping alcohol in excess, as, if these points be not attended to, the sulphuric acid will absorb the elements of water and produce **ethylene** (olefiant gas):—

$$C_2H_5HO + H_2SO_4 = H_2SO_4H_2O + C_2H_4.$$

The process is in theory continuous, but in practice is limited by the fact that after a time the sulphuric acid gets too weak to perform its work, owing to the water contained in the spirit used. The acid also slowly volatilizes, partly in the state of *oil of wine*. The actual process, as laid down by the B.P., is as follows:—

Mix ten fluid ounces of sulphuric acid with twelve fluid ounces of rectified spirit in a glass matrass capable of containing at least two pints, and, not allowing the mixture to cool, connect the matrass by means of a bent glass tube with a Liebig's condenser, and distil with a heat sufficient to maintain the liquid in brisk ebullition. As soon as the ethereal fluid begins to pass over, supply fresh spirit through a tube into the matrass in a continuous stream, and in such quantity as to equal the volume of the fluid which distils over. For this purpose use a tube furnished with a stopcock to regulate the supply, connecting one end of the tube with a vessel containing the spirit raised above the level of the matrass, and passing the other end through a cork fitted into the matrass. When thirty-eight fluid ounces of spirit have thus been added, and forty-two fluid ounces have distilled over, the process may be stopped. Dissolve ten ounces of calcium chloride in thirteen ounces of water, add half an ounce of slaked lime, and agitate the mixture in a bottle with the impure ether. Leave the mixture at rest for ten minutes, pour off the light supernatant fluid, and distil it with a gentle heat until a glass bead of specific gravtiy 0·735 placed in the receiver begins to float. The ether and spirit retained by the calcium chloride and by the residue of each rectification, may be recovered by distillation and used in a subsequent operation.

Thus made, ether contains about 10 per cent. of alcohol, and is a colourless,

very volatile, and inflammable liquid, emitting a strong and characteristic odour, and boiling below 105°. Specific gravity, 0·735. It evaporates without residue.

Crude ether is purified from alcohol and water by first shaking up with water, to dissolve out the alcohol, and then rectifying over a mixture of calcium chloride and freshly burned calcium oxide, to remove the water.

It is then found to have a specific gravity of ·720, and boils at 96° F.

Ethyl oxide burns with a white flame, yielding carbonic anhydride and water as the sole products of its combustion.

When a drop touches the skin, it evaporates so rapidly as to produce a sensation of extreme cold. It is only slightly soluble in water (1 ether in 10 of water), but is entirely miscible with alcohol. It is also an excellent solvent of oils and fats, as well as of phosphorus, scammony resin, quinine, mercuric and ferric chlorides, and many other bodies.

The vapour of ether is highly inflammable, and, when mixed with air, powerfully explosive.

$$\begin{array}{cccc} (C_2H_5)_2O + & 6O_2 & = 4CO_2 & + 5H_2O. \\ \text{2 vols.} & + \text{12 vols.} & = \text{8 vols.} & \end{array}$$

When passed through a red hot tube, it yields, among other products, ethene, methane, aldehyd, and acetylene. Ether kept in a badly stoppered vessel, rapidly becomes acid, owing to formation of acetic acid, thus:—

$$(C_2H_5)_2O + 2O_2 = 2C_2H_4O_2 + H_2O.$$

When ether is mixed with an equal volume of sulphuric acid, it produces sulphovinic acid:—

$$(C_2H_5)_2O + 2H_2SO_4 = 2C_2H_5.HSO_4 + H_2O.$$

III. COMPOUND ETHERS.

These include all salts other than haloids or oxides which an organic basylous radical can form with an acid, and correspond to the ordinary oxy salts of mineral chemistry. The acidulous radicals may be either organic or inorganic, but the basylous radicals must always be organic.

Compound ethers, generally, may be prepared by one or other of the following methods.

1. By the direct action of the acid upon the alcohol. Thus, oxalic acid heated with alcohol yields ethyl oxalate:—

$$2C_2H_5HO + H_2C_2O_4 = (C_2H_5)_2C_2O_4 + 2H_2O.$$

This process answers well for non-volatile acids of all kinds.

2. By distilling the alcohol with sulphuric acid and a sodium or potassium salt of the required acid. Example, acetic ether, B.P.:

$$C_2H_5HO + H_2SO_4 + NaC_2H_3O_2 = C_2H_5.C_2H_3O_2 + NaHSO_4 + H_2O.$$

This process is suitable for all volatile organic acids not decomposed by heating with H_2SO_4.

3. By double decomposition of the haloid ether of the required basylous radical with a silver salt of the required acidulous radical.

Example, the formation of ethene diacetate:—

$$C_2H_4Br_2 + 2AgC_2H_3O_2 = C_2H_4 2C_2H_3O_2 + 2AgBr.$$

The compound ethers are chiefly used as flavourings; and by various mixtures of their alcoholic solutions, the well known artificial essences of pears,

pineapples, etc., are produced. At the end of this work will be found a table, showing how these essences are manufactured. To go fully into the compound ethers would be beyond the scope of the present work, and we will therefore only consider a few of the salts of the leading radicals, which may be taken as typical of all the others.

Besides the neutral compound ethers we have acid compound ethers, such as ethyl hydrogen sulphate, which can themselves act as regular acids by exchanging their undisplaced hydrogen for metals or basylous radicals. Thus:—

Ethyl hydrogen sulphate, $C_2H_5.HSO_4$, or sulphovinic acid,
Ethyl sodium sulphate, $C_2H_5NaSO_4$, „ sodium sulphovinate.

(*a*) Compound Ethers of the Fatty Series $(C_nH_{2n+1})'R'$.

In considering these, we shall first take the official ones, and afterwards shortly glance at the remainder.

ETHYL NITRITE (SYN. **Nitrous Ether**). **Formula, $C_2H_5.NO_2$.**

This substance is produced by heating one part of starch with ten parts of nitric acid and passing the nitrous acid vapours thereby evolved into dilute alcohol kept cool in a two-necked bottle and connected with a well-cooled receiver. It is a pale yellow liquid with an apple-like odour, having a specific gravity of ·947 and boiling at 62° F. It is not used pure in Pharmacy, but is the chief ingredient in *spiritus etheris nitrosi*, B.P., which is essentially an impure solution of ethyl nitrite in alcohol with traces of aldehyd. It is prepared by distilling together alcohol, sulphuric acid, nitric acid, and copper wire. The reaction which takes place is somewhat complicated, but may be represented in one equation, as follows:—

$$C_2H_5HO + HNO_3 + H_2SO_4 + Cu = C_2H_5NO_2 + CuSO_4 + 2H_2O.$$

The use of copper is, doubtless, to cause an immediate commencement of the reaction, by at once reducing the nitric acid; but as the sulphuric acid is also present, it prevents the nitrate radical from combining with the copper, and sets it free to act upon the alcohol, the copper being found at the end of the process in the state of sulphate. If copper were not used, the nitric acid would be reduced by the alcohol only, and then a large quantity of aldehyd would be formed, thus:—

$$2C_2H_5HO + HNO_3 = C_2H_4O + C_2H_5NO_2 + 2H_2O.$$

For aldehyd is always formed when an oxidizing agent is reduced by alcohol. It has been found impossible to entirely prevent the formation of aldehyd, but the use of copper reduces the amount formed to a minimum.

In practice a pint of the spirit is mixed gradually with 2 ounces of sulphuric acid and 2½ ounces of nitric acid, and the whole is poured into a retort containing 2 ounces of fine copper wire and distilled at a temperature commencing at 170° F. but never exceeding 180° F., until 12 ounces have come over. Half an ounce more nitric acid is then added, and 3 ounces more distilled. The 15 ounces of strong solution of ethyl nitrite are then diluted for use by adding 2 pints of rectified spirit. *Spiritus ætheris nitrosi* thus made should be transparent and nearly colourless, with a very slight tinge of yellow; mobile, inflammable, of a peculiar penetrating apple-like odour, and sweetish, cooling, sharp taste. Specific gravity, 0·845. It effervesces feebly, or not at all, when shaken with a little sodium hydrogen-carbonate (presence in very small quantity, or entire absence of free nitrous and acetic acids). When agitated with a solution of ferrous sulphate and a few drops of sulphuric acid, it becomes deep

olive-brown or black (presence of nitrite). If it be agitated with twice its volume of saturated solution of calcium chloride in a closed tube, two per cent. of its original volume will separate in the form of ethyl nitrite and rise to the surface of the mixture.

Only $\frac{1}{5}$ of the whole of the ethyl nitrite separates on the addition of calcium chloride, therefore the two per cent. mentioned in the B.P. really corresponds to the ten per cent. of pure ethyl nitrite in the *spirit of nitrous ether*. The absence of free acid is shown by the non-effervescence with sodium hydrogen carbonate, and this is a test to which very few commercial specimens will answer. In practical dispensing, when specially prescribed with potassium iodide, it is most important to apply this test before using the spirit, as it would be likely to set free iodine (*see* **Action of Nitrites upon Hydriodic Acid**), and spoil the mixture. *Spirit of nitrous ether*, before being added to potassium iodide, should always be shaken up with a little potassium carbonate to prevent such accidents.

ETHYL ACETATE (Syn. *Acetic Ether*). **Formula, $C_2H_5.C_2H_3O_2$. Molecular Weight, 88.**

Produced by passing carbonic anhydride into an alcoholic solution of potassium acetate, the bye-product (potassium carbonate) being precipitated. The reaction is thus expressed:—

$$2KC_2H_3O_2 + 2C_2H_5HO + CO_2 = 2C_2H_5.C_2H_3O_2 + K_2CO_3 + H_2O.$$

The process adopted in the B.P. is the distillation of sodium acetate with alcohol and sulphuric acid, sodium hydrogen sulphate remaining, and ethyl acetate and water distilling over.

$$C_2H_5HO + NaC_2H_3O_2 + H_2SO_4 = C_2H_5.C_2H_3O_2 + NaHSO_4 + H_2O.$$

To the distilled product half its weight of calcium chloride is added in a stoppered bottle, and the whole having been allowed to remain together for twenty-four hours, the ethereal liquid is decanted and rectified.

Characters and Tests.—A colourless liquid with an agreeable ethereal odour. Specific gravity, 0·910. Boiling point, 166° F. Soluble in all proportions in rectified spirit and in ether. One part dissolves in 11 or 12 parts of water at 60° F.

According to Mr. Umney, the above statements are not correct, owing to the ether not being rectified over potassium carbonate, as should be done in order to remove acetic acid. He says:—

I had my suspicions that if I could find a specimen in pharmacy that would answer to the Pharmacopœia tests, I should in all probability find free acetic acid as an impurity. I also thought that some specimens might be contaminated with ordinary sulphuric ether.

Accordingly I examined three, with results as under:—

	Specific Gravity.	Boiling Point.	Free Acid.
A.	·890	160° F.	none.
B.	·889	158°	,,
C.	·915	164°	10 per cent. of monohydrated acetic acid.

Acetic ether is a good solvent of cantharidine, and is also, when mixed with ordinary ether, well adapted for taking up morphia in toxicological analyses. It is somewhat astonishing that the excellent process first mentioned has not been adopted officially.

ETHYL NITRATE (SYN. *Nitric Ether*). **Formula, $C_2H_5NO_3$.**

Is prepared by distilling alcohol with nitric acid in the presence of urea, to decompose any nitrous acid formed, and so prevent the formation of nitrite and aldehyd. It is insoluble in water, and has a specific gravity of 1·112, and boils at 186° F.

ETHYL SULPHATE. Formula, $(C_2H_5)_2SO_4$.

Prepared by passing the vapour of sulphuric anhydride into absolutely anhydrous ether. It is a colourless liquid, at once decomposed by the action of water into sulphovinic acid.

ETHYL HYDROGEN-SULPHATE (SYNS. *Ethyl-sulphuric Acid. Sulphovinic Acid*). **Formula, $C_2H_5HSO_4$.**

Is prepared by heating a mixture of **rectified spirit** and **sulphuric acid** to 212° F. :—

$$C_2H_5HO + H_2SO_4 = C_2H_5HSO_4 + H_2O.$$

When the mixture has cooled, it is freed from excess of acid by digestion with barium carbonate, and filtering out the barium sulphate formed. Barium sulphovinate remains in solution, and it is then carefully treated with dilute sulphuric acid, which precipitates barium sulphate, leaving pure ethyl hydrogen-sulphate in solution. As thus formed, sulphovinic acid, as it is usually termed, is a colourless, oily liquid, with an acid reaction, and having a specific gravity of 1·316. It decomposes slowly but spontaneously at ordinary temperatures, and when heated with alcohol to 250° F. it yields ether.

By dissolving oxides or carbonates of any desired metals in ethyl hydrogen-sulphate, a class of salts called **sulphovinates** is produced.

Sodium sulphovinate is prepared by decomposing barium sulphovinate with sodium carbonate. It is a white granular product, deliquescent, soluble in 0·7 parts of water at 60° F., and also soluble in alcohol. $BaCl_2$ in solution should throw down no precipitate.

ETHYL SULPHITE. Formula, $(C_2H_5)_2SO_3$.

Is a limpid liquid having a specific gravity of 1·085, forming alcohol and sulphurous acid when it comes in contact with water. It is formed by the action of sulphur dichloride, S_2Cl_2, or sulphur oxychloride, $SOCl_2$, on absolute alcohol.

ETHYL HYDROGEN-SULPHITE, or, more correctly, ETHYL SULPHONIC ACID. Formula, $C_2H_5HSO_3$, or $C_2H_5.SO_2.HO$.

Is formed by the action of sodium sulphite on ethyl iodide. It can form salts like sulphovinic acid. This is a specimen of a class of compounds of which an immense number have been discovered of late years.

The sulphonic acids are viewed as derived from sulphurous acid by the displacement of an atom of hydrogen by a basylous radical, thus :—

$SO_2{<}{}^{H}_{HO.}$	$SO_2{<}{}^{CH_3}_{HO.}$	$SO_2{<}{}^{CH_3}_{CH_3O.}$
(Sulphurous Acid.)	(Methyl Sulphonic Acid.)	(Methyl Methyl-sulphonate.)

The process given is a general one for preparing any sulphonic acid, but they may also be produced by oxidizing the hydrosulphides of the required

radical by nitric acid. They are so stable as not to be decomposed by boiling with potassium hydrate, but on being actually fused with solid KHO they evolve alcohol and yield potassium sulphite. By the action of nascent hydrogen, sulphonic acids yield hydrosulphides (mercaptans). Closely allied to the sulphonic acids are the acid hyposulphites called **sulphinic acids**, resulting from the displacement of hydrogen from hyposulphurous acid by a basylous radical, thus:—

$$SO{<}^{H}_{HO.} \qquad\qquad SO{<}^{CH_3}_{HO.}$$

(Hyposulphurous Acid.) (Methylsulphinic Acid.)

In making these latter compounds the zinc salt is first produced by acting on an organo-metallic body by sulphurous anhydride.

Example—zinc ethyl, thus treated, yields zinc ethyl sulphinite:—

$$Zn(C_2H_5)_2 + 2SO_2 = (C_2H_5SO_2)_2Zn.$$

ETHYL SULPHIDES.

Three of these compounds are known, as follows:—

NAME.	FORMULA.	BOILING POINT.	PREPARATION.
Ethyl monosulphide	$(C_2H_5)_2S$	196° F.	By passing ethyl chloride into an alcoholic solution of potassium sulphide.
Ethyl bisulphide	$(C_2H_5)_2S_2$	304°	By distilling ethyl oxalate with potassium bisulphide.
Ethyl trisulphide	$(C_2H_5)_2S_3$	450°	By a similar process with potassium pentasulphide.

ETHYL HYDROSULPHIDE (SYN. *Mercaptan*, or *Thio-alcohol*).
Formula, C_2H_5HS.

This body,—which is a limpid liquid, having a specific gravity of ·833, and boiling at 97°,—has perhaps the most horribly persistent and offensive odour of any known substance, something between sulphuretted hydrogen and garlic, but infinitely worse than either. To prepare it, strong alcoholic solution of potassium hydrate of 1·3 specific gravity is perfectly saturated with sulphuretted hydrogen, and the liquid thus obtained is distilled with an equal volume of solution of calcium ethyl sulphate (sulphovinate) of similar density. The heat used should be that of a bath of salt and water.

Mercaptan is very inflammable, yielding a bluish flame.

ETHYL PHOSPHATES.

There are three phosphates, the first two being produced by the direct action of syrupy phosphoric acid upon alcohol in varying proportions, and the last by double decomposition of argentic phosphate and ethyl iodide. All are liquids, and the first two can form metallic salts analogous to sulphovinates.

Monethyl hydrogen-phosphate (Phosphovinic acid).	$C_2H_5H_2PO_4$.
Diethyl hydrogen-phosphate	$(C_2H_5)_2HPO_4$.
Triethyl phosphate	$(C_2H_5)_3PO_4$.

ETHYL PHOSPHITES.

We have the neutral and acid phosphites, the latter called phosphonic acids, analogous to sulphonic acids.

ETHYL BORATE and ETHYL SILICATE. Formula, $(C_2H_5)_3BO_3$ and $(C_2H_5)_4SiO_4$.

Are both produced by the action of alcohol on the chlorides of boron or silicon. They are inflammable liquids, evolving when burned dense white fumes of boric and silicic anhydrides respectively.

ETHYL OXALATE, TARTRATE, CITRATE, etc.,

Are all made by the direct action of the specific acid upon alcohol.

AMYL NITRITE. Formula, $C_5H_{11}.NO_2$.

Is produced on heating starch and nitric acid, and passing the gas evolved into amyl hydrate. The latter body may be conveniently contained in a retort, and the liquid which passes over must be redistilled, and the portion distilling between 170° and 176° F. collected.

In this reaction ammonium nitrate is also produced, owing probably (according to N. Bunge) to the nitrous fumes formed being a mixture of N_2O_3 and N_2O_4:—

$$6C_5H_{11}HO + 3N_2O_3 + N_2O_4 = 6C_5H_{11}NO_2 + NH_4NO_3 + H_2O.$$

It may also be prepared by a similar process to *spiritus ætheris nitrosi*, using amylic instead of ethylic alcohol. The boiling point of PURE amyl nitrite is nearly 25 degrees lower than that given in the B.P., which thus describes it:—

Characters and Tests.—An ethereal liquid of a yellowish colour, and peculiar, not disagreeable odour. Specific gravity, 0·877. Boiling point, 205° F. Insoluble in water. Soluble in rectified spirit in all proportions.

If it be added drop by drop to caustic potash while fused by the application of heat, valerianate of potash will be formed.

The reaction with fused potassium hydrate is so violent as to frequently cause the production of flame. The vapours of amyl nitrite are orange coloured, and are used as an inhalation.

According to Professor Maisch, as usually prepared for pharmaceutical purposes, this body is exceedingly impure, and the author recommends the following method for obtaining a better product. Amyl alcohol, freed from ethyl alcohol by shaking with salt water and subsequent distillation, is mixed in a capacious retort with about an equal weight of nitric acid, and gently warmed till boiling commences, when the fire is withdrawn and the action allowed to complete itself. As soon as the thermometer rises above 100° the receiver is changed, and the distillate obtained below that temperature is shaken with caustic lime or its carbonate, and the oily liquid remaining is again distilled and the portion coming over between 96° and 100° collected as amyl nitrite.

AMYL ACETATE. Formula, $C_5H_{11}.C_2H_3O_2$.

Produced by distillation of a mixture of amyl hydrate, potassium acetate and sulphuric acid. The following equation represents the reaction which occurs:—

$$C_5H_{11}HO + KC_2H_3O_2 + H_2SO_4 = C_5H_{11}.C_2H_3O_2 + KHSO_4 + H_2O.$$

This is, when diluted with alcohol, the artificial essence of jargonelle pear. It is purified by digestion with calcium oxide and rectification over calcium chloride. It has a sp. gr. of about 864, is insoluble in water, soluble in amyl hydrate and ether, and slowly decomposed by potassium hydrate.

AMYL VALERIANATE. **Formula, $C_5H_{11}.C_5H_9O_2$.**

Is produced in the manufacture of valerianic acid. By the action of sodium hydrate it forms sodium valerianate and amyl hydrate, by double decomposition. It is an agreeably smelling oily liquid, used, when dissolved in alcohol, as an artificial essence of apple. The liquid which is mentioned in the B.P. as floating to the surface when the distillate obtained in the manufacture of sodium valerianate is neutralized, consists chiefly of this body.

CETYL PALMITATE (SYN. *Cetine*). **Formula, $C_{16}H_{33}.C_{16}H_{31}O_2$.**

Is the chief constituent of spermaceti (*cetaceum*, B.P.), and thus described :—

Nearly pure cetine, obtained, mixed with oil, from the head of the sperm whale, *Physeter macrocephalus*, *Linn.*, inhabiting the Pacific and Indian Oceans. It is separated from the oil by filtration and pressure, and afterwards purified.

Characters and Tests.—Crystalline, pearly white, glistening, translucent, with little taste or odour, reducible to powder by the addition of a little rectified spirit. Scarcely unctuous to the touch; does not melt under 100°.

It is easily dissolved by absolute alcohol, slightly by 87 per cent. alcohol, and not at all by water.

MELISSYL PALMITATE (SYNS. *Melissin. Palmitate of Myricyl*). **Formula, $C_{30}H_{61}.C_{16}H_{31}O_2$.**

The portion of bees and white wax which does not dissolve in boiling spirit is chiefly composed of this salt. Yellow wax is the prepared honeycomb of the hive bee. Its melting point is 140° F. When bleached, it forms white wax, which does not melt under 150° F.

(*b*) Compound Ethers of the Series $(C_nH_{2n})''R_2'$.

Are similar in formation to those of the fatty series.

(*c*) Compound Ethers of the Series $(C_nH_{2n-1})'''R_3'$, or Glycerides.

Under this head are included all the natural fats, which are compound ethers of the basylous radical glyceryl, $(C_3H_5)'''$, in combination with oleic, palmitic, or stearic acids. The chief ones may be represented as follows :—

Glyceryl oleate (*olein*, or *triolein*) . . .	$C_3H_53C_{18}H_{33}O_2$.
Glyceryl palmitate (*palmitin*, or *tripalmitin*) .	$C_3H_53C_{16}H_{31}O_2$.
Glyceryl stearate (*stearin*, or *tristearin*) . .	$C_3H_53C_{18}H_{35}O_2$.

The three classes are known, according to their consistence, as oils, butters, or tallows. Hundreds of different fats and oils are in common use, each of which varies in some respects from all others. As a rule, the odoriferous principles of fatty substances are due to admixtures, introduced into them from their sources, or in the course of their preparation, and not belonging to their essential constitution. The processes adopted for their purification are frequently very complicated. All natural fats contain a solid and a liquid constituent, but their relative amounts vary greatly; the preponderance of the

solid giving rise to a *tallow*, of the liquid to an *oil*, and a fairly equal amount of each forming a *butter*. The greater number of fats are produced by the replacement of more or less of the hydroxyl of glyceryl hydrate (glycerin, $C_3H_5 3HO$) by the palmitic, stearic, or oleic radicals, water being the bye-product.

As an example, we may instance the combination of stearic acid with glycerin to form "tristearin":—

$$C_3H_5 3HO + 3HC_{18}H_{35}O_2 = C_3H_5 3C_{18}H_{35}O_2 + 3H_2O.$$

From this it will be seen that the replacement is practically effected by the hydroxyl of the glycerin seizing upon the hydrogen of the acid, at the moment of liberation, to form water. The fat thus "synthesized" can be analyzed by the action of superheated steam (at 480° F.) which causes a simple reversal of the process:—

$$C_3H_5 3C_{18}H_{35}O_2 + 3H_2O = C_3H_5 3HO + 3HC_{18}H_{35}O_2.$$

The acidulous portion of a fat can only be separated from the basylous, so that both are obtained as an acid and a hydrate, respectively (their most stable forms), in the presence of water.

This breaking up of a fat is called **saponification**, and it can also be performed by boiling with an alkali or with an oxide and water. The result is, then, always the formation of a metallic salt of the fatty acid and the liberation of glycerin. Thus, taking the formation of ordinary soap from olive oil and sodium hydrate:—

$$C_3H_5 3C_{18}H_{33}O_2 + 3NaHO = 3NaC_{18}H_{33}O_2 + C_3H_5 3HO.$$

After boiling the oil and soda together until entirely dissolved, the addition of sodium chloride will cause the soap to float to the surface, leaving the glycerin in solution.

GLYCERYL TRIOLEATE (SYN. *Olein*). **Formula, $C_3H_5 3C_{18}H_{33}O_2$.**

Is the chief liquid constituent of all oils. If olive oil be cooled to 32° F. it deposits a quantity of solid fat, formerly called *margarin*, but now known to be chiefly palmitin with a little stearin; and the portion which remains liquid is nearly pure *olein*. This body, or its homologues, exists in all *non-drying* oils; on the other hand, the *drying* oils, such as linseed, poppy, hemp, etc., contain *linolein*, $C_3H_5 3C_{18}H_{27}O_2$; while castor oil contains *ricinolein*, $C_3H_5 3C_{18}H_{33}O_3$, which is a colourless oil, solidifying at 32° F. and yielding, when distilled with excess of potassium hydrate, octyl alcohol, from which artificial *essence of cognac*, or œnanthic ether, is manufactured.

GLYCERYL TRI-PALMITATE (SYN. *Palmitin*). **Formula, $C_3H_5 3C_{16}H_{31}O_2$.**

Is contained extensively in palm oil, is most common in fats in small quantities, and also in Chinese tallow and Japan wax. About 90 per cent. of the so-called *margaric acid* is palmitic acid. It is the more solid portion of palm oil, and is freed from the oily medium in which it is contained, by pressure, and successively treating the residue with boiling alcohol.

GLYCERYL TRISTEARATE (SYN. *Stearin*). **Formula, $C_3H_5 3C_{18}H_{35}O_2$.**

Is the chief portion of cacao and shea butters, and of beef and mutton suet and animal fats generally. It is a white crystalline solid fat, and exists in several modifications having various melting points, ranging from 125° F. to 156° F. It is used in making *sapo animalis*.

(*d*) Compound Aromatic Ethers.

PHENYL HYDROGEN-SULPHATE (SYN. *Sulphocarbolic Acid*).
Formula, $C_6H_5HSO_4$.

Is produced when **phenyl hydrate** (carbolic acid) is dissolved in strong sulphuric acid :—

$$C_6H_5HO + H_2SO_4 = C_6H_5HSO_4 + H_2O.$$

It gives rise to a class of salts called sulphocarbolates, which are now of medicinal interest. Their introduction is due to Dr. Sansom. Those of sodium, potassium, magnesium, calcium, iron, copper, and zinc have been prepared. Solution of ferric chloride strikes a ruby or violet tinge with these salts. They may all be prepared by direct solution of the oxide or carbonate of the desired metal in phenyl hydrogen-sulphate. The purification of the crude sulphocarbolic acid is conducted exactly as directed under ethyl hydrogen-sulphate. The great advantage of sulphocarbolates is, that they possess all the medicinal and antiseptic properties of carbolic acid without its unpleasant odour or its caustic character.

ZINC SULPHOCARBOLATE (SYN. *Phenyl Zinc Sulphate*).
Formula, $Zn(C_6H_5SO_4)_2$.

Produced by dissolving zinc oxide in sulphocarbolic acid :—

$$ZnO + 2C_6H_5HSO_4 = Zn(C_6H_5SO_4)_2 + H_2O\ ;$$

and then purified by crystallization from alcohol.

It is almost devoid of smell, and is soluble in water and in alcohol. In the formation of these salts the sulphocarbolic acid should be derived from chemically pure sulphuric acid (specific gravity 1·823) and carbolic acid (Calvert, No. 2).

CHAPTER XVIII.

ALDEHYDS, KETONES, PHOSPHINES, ETC.

I. ALDEHYDS.

THESE bodies are produced by the oxidation of alcohols, and may be viewed as the hydrides of the oxygenated radical corresponding to the alcohol radicals.

(*a*) Aldehyds from Monatomic Alcohols, $C_nH_{2n-1}O.H.$

These are all derived from the alcohol by the simple substitution of O for H_2. They are produced,—

1. By distilling the alcohol with an oxidizing agent.
2. By heating the calcium salt of the corresponding acid with calcium formate :—

$$Ca2C_2H_3O_2 + Ca2CHO_2 = 2C_2H_3O.H + 2CaCO_3.$$

3. They occur ready formed in some essential oils.

The aldehyd is usually named after the acid, and not the alcohol; thus, that from ethyl alcohol would be called **acetic aldehyd.** Aldehyds may be reconverted into the corresponding alcohols by the action of alkaline hydrates, a salt of the corresponding acid being simultaneously produced. Thus, benzoic aldehyd (oil of bitter almonds) yields benzyl hydrate and potassium benzoate when treated with potassium hydrate :—

$$2C_7H_6O + KHO = C_7H_7HO + KC_7H_5O_2.$$

Nascent hydrogen also reconverts aldehyds into alcohols. Example :—

$$C_2H_4O + H_2 = C_2H_5HO.$$

Aldehyds are characterized by all forming insoluble compounds with potassium acid sulphite; and this principle is taken advantage of in separating and obtaining them in a pure state. They are usually converted into the corresponding acid by simple exposure to the air.

(*b*) Aldehyds of the Fatty Series.

This series of bodies commences with formic aldehyd, CHO.H, and ends with Euodic aldehyd, $C_{11}H_{21}O.H.$

ACETIC ALDEHYD (SYN. *Acetyl Hydride*). **Formula, $C_2H_3O.H.$**

Is produced when alcohol is distilled with sulphuric acid and manganese peroxide, potassium dichromate, or potassium permanganate. The distillate is purified by precipitation with potassium hydrogen-sulphite and decomposition of the precipitate so obtained by sodium carbonate, when the pure

aldehyd separates and may be rectified over calcium chloride. It is a colourless liquid with a powerful ethereal odour, having a specific gravity of ·807 and boiling at 71° F. Exposed to the air, it changes to acetic acid; and this action takes place very rapidly in the presence of platinum black.

ACETAL. Formula, $C_6H_{14}O_2$, or C_3H_7O.

May be viewed as a compound of aldehyd with ethyl oxide, thus:— $C_2H_4O\,(C_2H_5)_2O$. It is a colourless liquid, having a specific gravity of ·821, and boiling at 219° F., and is produced, with other compounds, when alcohol is heated with aldehyd. It is obtained pure by passing hydrochloric acid gas into a solution of aldehyd in absolute alcohol and heating the compound thus formed with sodium ethylate.

TRICHLORALDEHYD (SYN. *Chloral*). **Formula, C_2HCl_3O.**

To understand the constitution of this body, it is necessary to remember that alcohol, subjected to the action of oxidizing bodies, such as we have seen chlorine to be, yields aldehyd, C_2H_4O. If we suppose three atoms of the hydrogen of the latter substance to be replaced by chlorine, we shall have *trichlorinated aldehyd*, or *trichloraldehyd*, or chloral, C_2HCl_3O.

It is prepared by causing a continuous stream of perfectly dry chlorine to pass through absolute alcohol as long as absorption takes place. The process, which takes many hours and even days, is first conducted in the cold; but, towards the end the temperature is gradually increased to the boiling point. This yields crude chloral, which is purified by digestion with three times its bulk of strong sulphuric acid. The chloral, which rises to the top, having been drawn off, is redistilled; and this having been repeated several times, the last product is distilled from calcium oxide. Thus prepared, chloral is an oily colourless liquid having a density of 1·502. It is used to prepare,—

CHLORAL HYDRATE. Formula, $C_2HCl_3O.H_2O$.

Which is produced by adding a very little water to the chloral prepared as above. On thus mixing, great heat is evolved, and the chloral hydrate is formed, which crystallizes in plates or needles of great brilliancy, emitting a peculiar odour, and possessing an exceedingly disagreeable taste. To take the simplest view of the whole reactions:—

$$C_2H_5HO + 4Cl_2 = C_2HCl_3O + 5HCl.$$
$$C_2HCl_3O + H_2O = C_2HCl_3O.H_2O.$$

This equation, however, does not represent the actual reactions which take place, nor does it account for the formation of the intermediate products which are formed on prematurely arresting the process.

The following equations, we believe, satisfy all requirements.

The first action results in the formation of aldehyd:—

$$C_2H_6O + Cl_2 = C_2H_4O + 2HCl.$$

In the second, *mono-chlor-ether* forms:—

$$2C_2H_4O + 2C_2H_6O + 2HCl = 2C_2H_5(C_2H_4Cl)O + 2H_2O.$$

From the third, *tetra chlor-ether* results:—

$$2C_2H_5(C_2H_4Cl)O + 6Cl_2 = 2C_2H_5(C_2HCl_4)O + 6HCl.$$

Fourthly, chloral is formed, together with alcohol and hydrochloric acid:—

$$C_2H_5(C_2HCl_4)O + H_2O = C_2HCl_3O + C_2H_6O + HCl.$$

Chloral hydrate is a translucent solid, and in reality is only hydrated chloral, *i.e.*, chloral combined with water of crystallization; not a true hydrate, which consists of a metal or basylous radical combined with hydroxyl. The chlorine in chloral is not combined as in chlorides generally, no precipitate falling on the addition of argentic nitrate. Hydrated chloral may be sublimed without decomposition, and forms a white mass of small powdery crystals, which fuse at about 111° F., and volatilize at 208° F. The fused mass commences to solidify at 120° F., and if the chloral be mixed with fragments of broken glass, it will begin to boil at 205° F. It dissolves bromine, phosphorus, and iodine, forming a purplish solution with the latter. After a time hydrated chloral has been stated to lose its solubility in water; but this property can be restored to it by sublimation, or digestion with water. In contact with the blood, and also with alkaline hydrates, it yields chloroform, the slow formation of which secures a more lasting effect than the use of the latter itself.

The action of potassium, ammonium, and calcium hydrates produces formates and chloroform, thus:—

$$C_2HCl_3O + KHO = KCHO_2 + CHCl_3.$$

The calcium hydrate is used to effect this reaction when it is employed in determining the value of samples of chloral hydrate, as it gives the most reliable results, through the action being less violent, and therefore less liable to be complicated by the formation of the products arising from an excess of alkaline hydrate. These are chloride and formate, and are produced as shown below:—

$$CHCl_3 + 4KHO = 3KCl + KCHO_2 + 2H_2O.$$

The estimation is conducted in a flask, into which are put 30 grains of calcium hydrate and 100 grains of chloral hydrate, with an ounce of water. A long tube kept cool by any convenient means is adapted to the flask, the other end passing into a small weighed bottle (such as a specific gravity bottle with a stopper), which is kept at as low a temperature as may be found practicable. The heat, which is to be applied to the flask when all is complete, should not exceed 180° F. When chloroform ceases to come over, the weight of the contents of the bottle should not be less than 70 grains.

Chloral can act upon hydrates of such radicals as ethyl to form substances resembling its hydrate. Of these bodies, termed "alcoholates," the one obtained from ethyl hydrate is alone important. It is a white solid, crystallizing in clear needles, which, unlike the hydrate, turns sulphuric acid brown. Nitric acid of 32 per cent. (1·2 sp. gr.) gives abundant fumes when warmed with the alcoholate, none when the hydrate is substituted.

(*c*) Aldehyds of the Acrylic Series, $C_nH_{2n-3}O.H$.

These are derived from their alcohols in a similar manner to the aldehyds already studied, but are unsaturated compounds capable of combining with two equivalents of a monad element or radical.

ACRYLIC ALDEHYD (SYN. *Acroleïn*). **Formula, $C_3H_3O.H$, or C_3H_4O.**

Is the cause of the irritating odour always accompanying the destructive distillation of fats containing glycerin. It is prepared by heating glycerin with strong sulphuric acid, which acts as a dehydrating agent, thus:—

$$C_3H_53HO - 2H_2O = C_3H_4O.$$

It is a highly volatile and intensely irritating liquid, freely soluble in alcohol and ether, but sparingly in water.

CROTONIC ALDEHYD. Formula, $C_4H_5O.H$, or C_4H_6O.

Is supposed to be produced from acetic aldehyd by a process of duplication in the manufacture of—

TRICHLORCROTONIC ALDEYHYD (SYN. *Croton Chloral*). **Formula, $C_4H_3Cl_3O$.**

Which is prepared by passing chlorine into acetic aldehyd in a manner similar to that already described under chloral.

The first action has been viewed as a simple condensation of the aldehyd molecule with elimination of water, thus :—

$$2C_2H_4O = C_4H_6O + H_2O.$$

then the substitution of chlorine for hydrogen takes place in the crotonic aldehyd formed :—

$$C_4H_6O + 3Cl_2 = C_4H_3Cl_3O + 3HCl.$$

In contact with alkalies, it is supposed to form allyl chloroform and a formate, thus :—

$$C_4H_3Cl_3O + KHO = C_3H_3Cl_3 + KCHO_2.$$

It has been recommended as a substitute for ordinary chloral.

Lately this compound has been found to be really butyric chloral, $C_4H_5Cl_3O$, or trichlorobutyric aldehyd, and that the original name of croton chloral is a misnomer; but it is still sold as such. Its hydrate resembles ordinary chloral hydrate in appearance.

(*d*) Aromatic Aldehyds.

BENZOIC ALDEHYD (SYNS. *Oil of Bitter Almonds. Benzoyl Hydride*). **Formula, $C_7H_5O.H$.**

Results from the distillation of bitter almonds with water, owing to the transformation of amygdalin (contained in bitter, but not in the sweet, almonds) by a ferment (found in both varieties) termed emulsin, or synaptase. The representation of the reaction is usually as follows :—

$$C_{20}H_{27}NO_{11} + 2H_2O = HCN + C_7H_5O.H + 2C_6H_{12}O_6.$$

The pure hydride can be produced by the distillation of that contaminated with hydrocyanic acid with calcium hydrate and ferrous chloride, calcium ferrocyanide or ferrous ferrocyanide being formed, according as calcium or ferrous salts predominate. Like all true aldehyds, it forms a definite crystallizable compound with sodium hydrogen sulphite, which, after washing and decomposition with sodium carbonate, yields the purified oil of bitter almonds. Water takes up nearly $3\frac{1}{2}$ per cent. of benzoic aldehyd, and it is also perfectly miscible with alcohol and ether. When free from hydrocyanic acid, *it is devoid of poisonous properties*. The crude essential oil of bitter almonds consists of benzol hydrate contaminated with benzimide, benzoine, and benzoic acid.

The first results from the combination of hydrocyanic acid with benzoyl aldehyd. If this be treated with alcohol, the benzimide is extracted, and when obtained in the solid state, may be recognised by adding strong sulphuric acid, which forms a green (or sometimes bluish) solution, becoming converted to red by standing.

The second (benzoine) is a polymeric form of the essential oil, which becomes purplish by the action of sulphuric acid. Its formula is the double of that body, and hence it is regarded as isomeric with benzyl benzoate, thus :—

$$2C_7H_5O.H = C_7H_7(C_7H_5O_2) = C_{14}H_{12}O_2.$$

It sometimes receives the denomination of *camphor of bitter almond oil.* When a strong heat is employed in the preparation or purification of the oil, more benzoine is formed than is otherwise the case, and the product has higher specific gravity. The crude oil yields a dark-red liquid on adding strong sulphuric acid, which loses its colour, becoming converted into an opalescent yellowish liquid upon the addition of water. The ordinary percentage of hydrocyanic acid in the impure aldehyd is 8 per cent., but it may contain as much as $14\frac{1}{2}$ per cent. Ether and alcohol act as complete solvents of the benzoyl hydride and its usual impurities. The formation of benzoic acid occurs in the oil slowly by spontaneous oxidation, but is said to take place least readily if the oil be free from moisture. The essence of bitter almonds is usually composed of pure benzoyl hydride diluted to one-fourth strength with alcohol. It may be tested for hydrocyanic acid,—from which it is obvious that it should be perfectly free,—by any of the methods for the detection of that body, of which, in this case, the *sulphur test* is probably the best.

(*See Author's* **Analytical Chemistry**, *page* 64.)

CINNAMIC ALDEHYD (SYNS. *Cinnamyl Hydride. Essential Oil of Cinnamon*). **Formula, $C_9H_7O.H$.**

Is prepared by heating essential oil of cinnamon, the major portion of which is this hydride, with a strong solution of potassium hydrogen-sulphite; separating the crystals, drying the filter containing them by exposure to the air, reducing to powder, washing with alcohol, re-drying, dissolving in warm dilute sulphuric acid, allowing the mixture to stand, and drawing off the cinnamyl hydride which rises to the surface. Some slight impurities existing in it may be removed by agitation with water and drying the washed product.

It is a colourless liquid, converted more or less rapidly into cinnamic acid, and consequently acquiring an acid reaction by exposure to the air. Nitric acid forms a solid compound which, when separated from the liquid by pressure, yields a pure oil on solution in water, by which it is decomposed.

By atmospheric oxidation it gives birth not only to cinnamic acid but also to a resin. A substance exists which is isomeric with cinnamyl hydride. It is termed styracin, or meta-cinnamein; and results from the treatment of balsam of Peru with a solution of potassium hydrate in alcohol. The cinnamic aldehyd, possessing an odour of cinnamon, is readily distinguished by the sense of smell from benzoyl aldehyd. It assumes a green colour on passing into it a little hydrochloric acid gas.

II. KETONES.

These bodies are the result of the oxidation of secondary alcohols. They may be regarded as compounds of a basylous radical with the oxygenated radical immediately above it in carbon value, or as being aldehyds in which H has been displaced by a basylous radical, thus :—

Acetic aldeyd . .	$C_2H_3O.H.$
Acetic ketone, or acetone	$C_2H_3O.CH_3.$

They are also viewed by some as compounds in which the dyad carbonyl, CO, is saturated by two monad basylous radicals thus :—

$$CO.(CH_3)_2.$$

They may all be prepared by heating the calcium salt of the corresponding fatty acid.

ACETONE, C_3H_6O (SYNS. *Acetic Ketone*, $C_2H_3O.CH_3$. *Dimethyl Ketone*, $CO(CH_3)_2$).

Is produced by the heating of any acetate, preferably calcium acetate ; and is also one of the products of the dry distillation of wood. It is a colourless, limpid liquid, having a characteristic odour, a specific gravity of ·792, and boiling at 131° F. It is miscible with alcohol, ether, and water, and is inflammable, burning with a bright flame.

III. PHOSPHINES, ARSINES, AND STIBINES.

These bodies are analogous to the amines, and result from the displacement of hydrogen from PH_3, AsH_3, and SbH_3, respectively, by basylous radicals. They act as bases, combining with acids to form salts, and are as a rule liquids with a powerful odour and very inflammable.

They are not used in medicine, but as examples we may quote :—

NAME.	FORMULA.	BOILING POINT.	PREPARATION, ETC.
Triethylphosphine	$P(C_2H_5)_3$	261·5° F.	By the action of phosphorous chloride on zinc ethyl.
Triethylarsine	$As(C_2H_5)_3$	284·0°	By the action of ethyl iodide on an alloy of arsenic and sodium.
Triethylstibine	$Sb(C_2H_5)_3$	316·4°	By the action of ethyl iodide on an amalgam of antimony and potassium.

Arsenic also forms with organic radicals unsaturated compounds of a basylous nature, but not on the ammonia type, and therefore to be distinguished from true arsines. The most remarkable of these bodies is,—

ARSEN DIMETHYL (SYN. *Cacodyl*, $As(CH_3)_2$; *in the free state*, $As_2(CH_3)_4$).

This is a very offensive and terribly poisonous liquid, boiling at 338° F., and freezing at 42·8° F. which, when poured out into the air, immediately takes fire and liberates arsenic. It is prepared by first distilling together arsenious anhydride and potassium acetate, when a product is obtained which is cacodyl oxide, and is called alkarsin, or Cadet's fuming liquid.

$$4KC_2H_3O_2 + As_2O_3 = As_2(CH_3)_4O + 2K_2CO_3 + 2CO_2.$$

This liquid, which is spontaneously inflammable, is converted into the chloride by the action of hydrochloric acid ; and from the latter compound the pure cacodyl is produced by distillation with metallic zinc.

$$As_2(CH_3)_4Cl_2 + Zn = As_2(CH_3)_4 + ZnCl_2.$$

The salts of cacodyl are all poisonous, but more especially cacodyl cyanide, which is prepared by the action of cacodyl oxide on mercuric cyanide. On exposure this body is at once decomposed, giving both arsenic and hydrocyanic acid. When, however, cacodyl is permitted to oxidize in the presence of moisture, a compound called cacodylic acid is produced, $As(CH_3)_2O.HO$, which differs from all the rest in not taking fire in the air, and not being poisonous.

IV. ORGANO-METALLIC BODIES.

Are compounds of an alcohol radical with a metal other than a pentad. They are of the greatest use to the scientific chemist, many of the most interesting syntheses having been conducted through them. They may be produced by the direct action of the required metal or its sodium alloy on the iodide of the required radical. As a distinctly typical compound of this class we may glance at—

ZINC-ETHYL (SYN. *Zinc Ethide*). **Formula, $Zn(C_2H_5)_2$.**

This is a very volatile liquid, which takes fire on coming in contact with the air, producing copious fumes of zinc oxide. It has a disagreeable odour, boils at 244° F., and has a specific gravity of 1·182. It is produced by heating ethyl iodide with zinc in a sealed tube. The first action is the formation of a white crystalline mass of zinc ethiodide, thus :—

$$2C_2H_5.I + Zn_2 = 2Zn(C_2H_5).I.$$

The contents of the tube are then distilled in an atmosphere of hydrogen, when the zinc-ethyl is formed and distils over, leaving zinc iodide in the retort :—

$$2Zn(C_2H_5).I = Zn(C_2H_5)_2 + ZnI_2.$$

When brought into contact with water, zinc-ethyl instantly decomposes into zinc hydrate and ethane, thus :—

$$Zn(C_2H_5)_2 + 2H_2O = Zn2HO + 2C_2H_6.$$

By the action of carbonic anhydride, organo-metallic bodies are transformed into salts of the fatty acid immediately above in carbon value.

For example, zinc ethide, thus treated, yields zinc propionate :—

$$Zn(C_2H_5)_2 + 2CO_2 = Zn2C_3H_5O_2.$$

On the other hand, the action of carbonous oxide produces ketones. Thus, sodium methide yields acetone under the influence of carbonous oxide.

$$2NaCH_3 + CO = CH_3.C_2H_3O + Na_2.$$

CHAPTER XIX.

AMMONIA DERIVATIVES.

In addition to the ammonium salts already studied, ammonia can also form an immense group of bodies by the substitution of radicals, either acid or basylous, for one or more atoms of its hydrogen. This may take place with one or more molecules of ammonia, thus (R′ being any monad radical) :—

$$N\begin{cases}H\\H\\H\end{cases}\quad N\begin{cases}R'\\H\\H\end{cases}\quad \text{or } N\begin{cases}R'\\R'\\H\end{cases}\quad \text{and even } N\begin{cases}R'\\R'\\R'\end{cases}$$

or with a double molecule (R″ being a dyad radical) :—

$$N_2\begin{cases}H_2\\H_2\\H_2\end{cases}\quad N_2\begin{cases}R''\\H_2\\H_2\end{cases}\quad N_2\begin{cases}R''\\R''\\H_2\end{cases}\quad N_2\begin{cases}R''\\R''\\R''\end{cases}$$

and so on through the types $N_3\begin{cases}H_3\\H_3\\H_3\end{cases}\quad N_4\begin{cases}H_4\\H_4\\H_4\end{cases}$ etc.

I. AMIDES.

When the displacing radical is acidulous, the compound is called an **amide**, and we have—

1. Monamides.

In which one molecule of ammonia has its hydrogen replaced to a greater or less extent. When one atom only is displaced, the resulting compound is a *primary monamide:* example, acetamide, $N\begin{cases}(C_2H_3O)'\\H_2\end{cases}$. When two atoms are displaced, we have a *secondary monamide:* example, diacetamide, $N\begin{cases}(C_2H_3O)_2'\\H\end{cases}$. Lastly, a *tertiary monamide* would be produced by the entire displacement of the whole three atoms of H: example, ethyl-diacetamide, $N\begin{cases}(C_2H_5)'\\(C_2H_3O)_2'\end{cases}$. In the latter case the displacement of H is partly accomplished by a non-oxygenated (basylous) radical, and such a compound is called an **alkalamide**.

Primary Monamides, if volatile, are best prepared by heating the ammonium salt of the required acid radical : example,—

$$NH_4C_2H_3O_2 = C_2H_3O.NH_2 + H_2O.$$

but they may also be prepared by heating a compound ether of the required radical with an alcoholic solution of ammonia. Thus, ethyl acetate by this process will yield acetamide, and form alcohol :—

$$C_2H_5C_2H_3O_2 + NH_3 = C_2H_3O.NH_2 + C_2H_5HO.$$

Insoluble monamides are best prepared by the ac anhydride of the required acid, or the chloride of th for simplicity, to the same amide, we have—

$$(C_2H_3O)_2O + 2NH_3 = C_2H_3O.NH_2 + N$$
$$C_2H_3O.Cl + 2NH_3 = C_2H_3O.NH_2 + N$$

FORMAMIDE. Formula, $CHO.NH_2$.

Is a liquid soluble in water and alcohol, and con phosphoric anhydride into hydrocyanic acid or formon

ACETAMIDE. Formula, $C_2H_3O.NH_2$.

Is a crystalline solid, melting at 172·5° Fahr., solubl and resolved by the addition of water into ammonia heated with a strong acid or alkali.

Secondary Monamides are produced from the prim of dry hydrochloric acid at an elevated temperature. yields diacetamide :—

$$2C_2H_3O.NH_2 + HCl = (C_2H_3O)_2NH +$$

Alkalamides are formed by heating a compound instead of ammonia. Thus, by heating ethyl acetate w ethyl-acetamide :—

$$C_2H_5.C_2H_3O_2 + C_2H_5.NH_2 = N\begin{cases}(C_2H_5)' \\ (C_2H_3O)' \\ H\end{cases} + C_2H_5HO.$$

Tertiary Monamides are produced by the action of an acid chloride on an alkalamide ; thus, acetyl chloride and ethyl-acetamide yield ethyl diacetamide and hydrochloric acid.

2. Diamides.

Result from the displacement of hydrogen from two molecules of ammonia by a dyad oxygenated (acid) radical. They are best prepared by heating the ammonium salt of the required radical. Thus, by heating ammonium oxalate, we obtain oxamide :—

$$(NH_4)_2C_2O_4 = C_2O_2.N_2H_4 + 2H_2O ;$$

or, by the action of ammonia on a compound ether of the required acid, as in the case of tartramide, prepared by heating ethyl tartrate with ammonia, thus :—

$$(C_2H_5)_2'C_4H_4O_6 + 2NH_3 = C_4H_4O_4.N_2H_4 + 2C_2H_5HO.$$

UREA (SYN. *Carbamide*). **Formula,** $N_2\begin{cases}CO \\ H_2 \\ H_2\end{cases}$; *or* $CO''.N_2H_4$.

Exists in the urine, and is derived from the oxidation of the nitrogenous tissues of the animal system, of which it is one of the final products. It may be isolated from urine by simple evaporation, extraction of the residue by alcohol, and recrystallization, also from strong alcohol. But it may be also prepared by synthesis, directly from its elements ; because it has been formed by simply heating ammonium cyanate, which then changes into urea.

During this change it loses nothing, and it is therefore a simple rearrangement of the elements of the molecule :—

$$NH_4CNO = N_2\left\{\begin{array}{l}CO\\H_2\\H_2\end{array}\right.$$

Ammonium Cyanate = Urea.

In practice, artificial urea is made by fusing together potassium cyanide and red lead, dissolving in water, adding ammonium sulphate, evaporating to dryness, and extracting the urea with boiling alcohol, which does not dissolve the potassium sulphate formed.

1. $KCN + Pb_3O_4 = KCNO + 3PbO.$
2. $2KCNO + (NH_4)_2SO_4 = 2CO''.N_2H_4 + K_2SO_4.$

When urine is evaporated to dryness, and the alcoholic extract of the residue is treated with nitric acid and evaporated, it deposits crystals of urea nitrate, which are well defined under the microscope.

Urea crystallizes in colourless 4-sided prisms soluble in water and alcohol. Heated, it gives off ammonia and is converted into cyanuric acid. (*See* **Cyanates**, *page* 183.)

3. Triamides.

Are derived from three molecules of ammonia, and an example of them is found in *citramide*, which is a crystalline solid, obtained by the action of alcoholic ammonia upon ethyl citrate.

$$(C_2H_5)_3C_6H_5O_7 + 3NH_3 = C_6H_5O_4.N_3H_6 + 3C_2H_5HO.$$

4. Amic Acids.

Are monamides in which one hydrogen has been displaced by a dyad oxygenated radical having one of its atomicities saturated by hydroxyl, thus :—

Ammonia.	Monamide.	Amic Acid.
$N\left\{\begin{array}{l}H\\H\\H\end{array}\right.$	$N\left\{\begin{array}{l}(C_2H_3O)'\\H\\H\end{array}\right.$	$N\left\{\begin{array}{l}(CO''.HO')'\\H\\H\end{array}\right.$

They are produced by heating the acid instead of the normal ammonium salt of the required radical. For example, we have seen that ammonium oxalate, heated, yields *oxamide;* but if we heat ammonium hydrogen oxalate, we obtain **oxamic acid.** Thus, comparing the two reactions, we have :—

$$(NH_4)_2C_2O_4 = N_2\left\{\begin{array}{l}(C_2O_2)''\\H_2\\H_2\end{array}\right. + 2H_2O.$$

$$NH_4HC_2O_4 = N\left\{\begin{array}{l}(C_2O_2.HO)'\\H\\H\end{array}\right. + H_2O.$$

The only one of interest in pharmacy is—

CARBAMIC ACID. Formula, $(CO.HO)'NH_2$.

This compound is not known in the free state, but it acts as a monad acid having one atom of H replaceable by a base and leaving $(NH_2CO_2)'$ as the radical of a class of salts called **carbamates.** Ammonium carbamate, $NH_4.NH_2CO_2$, may be prepared by passing dry carbonic anhydride and ammonia into absolute alcohol, and heating the crystalline precipitate thus formed in a sealed

tube to 220° Fahr. Ammonium carbamate forms in bold crystals, which, when further heated in a sealed tube to 280° Fahr., are converted into urea and normal ammonium carbonate.

$$2NH_4NH_2CO_2 = CO.N_2H_4 + (NH_4)_2CO_3.$$

It exists in official *carbonate of ammonia* (*see page* 142).

II. AMINES.

When the radical displacing the hydrogen from ammonia is basylous, the resulting compound is called an **amine**; and we can have an exactly similar arrangement of *amines* to those we had of *amides*, viz.:—

Primary.	Secondary.	Tertiary.
$N\left\{\begin{matrix}C_2H_5\\ H\\ H\end{matrix}\right.$	$N\left\{\begin{matrix}C_2H_5\\ C_2H_5\\ H\end{matrix}\right.$	$N\left\{\begin{matrix}C_2H_5\\ C_2H_5\\ C_2H_5\end{matrix}\right.$
(Ethylamine).	(Diethylamine).	(Triethylamine).

Amines are powerful bases, and can unite with acids to form salts. Their behaviour in this respect is, however, that of ammonia, $(NH_3)''$, and not of ammonium, $(NH_4)'$. Thus, the ordinary compound of hydrochloric acid and ammonia may be viewed in two lights,—

1. As ammonium chloride, $(NH_4)'Cl'$, in which the hydrogen of the HCl unites with the ammonia to form the basylous radical $(NH_4)'$, which then joins with the chlorine to form a salt.

2. But the same compound may be considered to be hydrochlorate of ammonia, $(NH_3)''.H'Cl'$, in which the NH_3 joins with the entire HCl, and the nitrogen simply exercises its full pentad atomicity instead of its latent triad, thus:—

(Ammonia).

(Ammonia Hydrochlorate).

It is on this latter type that the salts of amines are based; and therefore, instead of speaking of ethylamine iodide, we call it ethylamine hydriode, and write it $NH_2(C_2H_5)'.HI$, etc.

1. Monamines.

These bodies may be produced by heating the iodide of a non-oxygenated (basylous) radical with alcoholic ammonia to 212° in a sealed tube, and then distilling the resulting hydriodide of the amine with potassium hydrate.

Thus by this treatment we obtain *ethylamine*:—

$$C_2H_5I + NH_3 = NH_2(C_2H_5)'.HI.$$
$$NH_2(C_2H_5)'.HI + KHO = NH_2(C_2H_5)' + KI + H_2O.$$

By repeating the process, using the primary amine instead of ammonia, we get *diethylamine*:—

$$C_2H_5I + NH_2(C_2H_5) = NH(C_2H_5)_2'.HI.$$
$$NH(C_2H_5)_2.HI + KHO = NH(C_2H_5)_2' + KI + H_2O.$$

By again repeating the process with the secondary amine, we obtain *triethylamine*:—

$$C_2H_5I + NH(C_2H_5)_2 = N(C_2H_5)_3'.HI.$$
$$N(C_2H_5)_3.HI + KHO = N(C_2H_5)_3' + KI + H_2O.$$

By regulating the proportions of the iodide and the alcoholic ammonia, either of the amines may be at once obtained, without going all through the above steps; but the primary, secondary, and tertiary compounds, if mixed, cannot be separated by fractional distillation. The lowest possible amine, namely, **methylamine**, $NH_2(CH_3)'$, is a colourless gas, and is of all known gaseous bodies the most soluble in water. **Trimethylamine**, $N(CH_3)_3'$, isomeric with **propylamine**, $NH_2(C_4H_7)'$, is a very volatile liquid, existing to a large extent in herring pickle and in cod's liver, the disgusting odour of both of which is due to its presence. It is found also in small quantities in cod liver oil, and is formed when codeine and narcotine are distilled with potassium hydrate.

It is also evolved when atropine is heated with potassium dichromate and sulphuric acid, and the resulting solution heated with potassium hydrate.

ETHYLAMINE. Formula, $NH_2(C_2H_5)'$.

Is a colourless liquid with a strongly ammoniacal smell, boiling at 66° Fahr., and emitting an inflammable vapour.

DIETHYLAMINE. Formula, $NH(C_2H_5)_2$.

Is also a colourless liquid, very alkaline, and boiling at 158·5° F.

TRIETHYLAMINE. Formula, $N(C_2H_5)_3$.

Resembles the former compound, but boils at 192° F.

When mixed with dry ethyl iodide, a powerful reaction ensues, and a white crystalline mass of **tetrethyl-ammonium iodide** is formed :—

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I.$$

This salt is soluble in water, and when a solution is shaken up with freshly precipitated argentic oxide and filtered, a colourless liquid called **tetrethyl-ammonium hydrate**, $N(C_2H_5)_4HO$, is formed. This liquid is strongly alkaline, may be boiled without decomposition, and remarkably resembles *liquor potassæ* in all its reactions, even to the extent of precipitating the same metals. By neutralizing this fluid with acids, the other salts of tetrethyl-ammonium may be prepared.

PHENYLAMINE (SYN. *Aniline*). **Formula, $N\begin{cases}C_6H_5\\H\\H\end{cases} = C_6H_7N$.**

This body, in which one atom of the hydrogen of ammonia has been displaced by the basylous radical **phenyl**—(C_6H_5)—is produced in immense quantities by the reduction of nitrobenzene. This reduction is usually effected by nascent hydrogen, by adding the nitrobenzene to zinc and sulphuric acid, or more commonly, on the large scale, to iron and acetic acid; then separating the aniline formed by distillation :—

$$C_6H_5NO_2 + 3H_2 = C_6H_7N + 2H_2O.$$

Aniline is an oily, colourless liquid, sparingly soluble in water, but freely in alcohol and ether. It has a specific gravity of 1·036 at 32°, and boils at 364° F.

By oxidation aniline yields the splendid *mauve* and similar colours with which we are now so familiar, their origin being due to our talented countryman, Mr Perkin. The oxidants employed in the arts are very numerous; but in applying the reaction for the testing of aniline, we generally employ *chlorinated lime* or potassium chlorate. (*See* **Nitrobenzene.**)

The following are some of the chief aniline dyes :—

1. *Mauve*, or aniline purple, is the sulphate of a base called *mauveine*, $C_{26}H_{24}N_4$, and is prepared by the action of potassium dichromate on aniline sulphate.

2. *Magenta*, or aniline red, is a base called *rosaniline*, $C_{20}H_{19}N_3$, is prepared by heating aniline with arsenic acid. This product is usually dissolved in water, precipitated by sodium hydrate, and the precipitate dissolved in acetic acid, thus forming acetate of rosaniline, which is the *roseine* of commerce.

3. *Blue* and *violet* are obtained by acting on rosaniline with excess of aniline; and the latter is also made by acting on rosaniline with ethyl iodide, forming triethyl-rosaniline hydriodide.

4. *Green* is produced from magenta by heating with aldehyd and sulphuric acid.

5. *Black* is produced by acting on aniline with potassium chlorate and cupric sulphate. It is absolutely indestructible, and many of the newer marking inks are simply made with aniline hydrochlorate, potassium dichromate, and cupric sulphate. They have, however, a tendency to rot the fabric unless very carefully made.

2. Diamines.

These are derived from two molecules of ammonia, the hydrogen of which is displaced by dyad basylous radicals. They are prepared like monamines, using the haloid ether of a dyad radical. Thus, ethene diamine is a colourless liquid, boiling at 255° Fahr., which is prepared by heating ethene bromide in a sealed tube with alcoholic ammonia, and distilling with potassium hydrate:—

$$C_2H_4Br_2 + 2NH_3 = N_2H_4(C_2H_4)''2HBr.$$
$$N_2H_4(C_2H_4)''.2HBr + 2KHO = N_2H_4(C_2H_4)'' + 2H_2O + 2KBr.$$

The secondary and tertiary diamines are formed, like the corresponding monamines, by repeating the process, using the diamine instead of ammonia.

Besides the *Diamines* we can have—

$$\textit{Triamines from } N_3\left\{\begin{matrix}H_3\\H_3\\H_3\end{matrix}\right.$$

$$\text{Also } \textit{Tetramines from } N_4\left\{\begin{matrix}H_4\\H_4\\H_4\end{matrix}\right.$$

To the latter class, doubtless, belong several alkaloids, such as caffeine, ($C_8H_{10}N_4O_2$), and theobromine, ($C_7H_8N_4O_2$), but the constitution of their molecules is not yet discovered. There are many similar bodies of which we are still unable to fix the exact constitution, and, whether *amides* or *amines*, we call them **compound ammonias**. Berzelius was the first to point out that all the alkaloids, which constitute the active constituents of so many articles of *materia medica* derived from the vegetable kingdom, were probably only compound ammonias. A few alkaloids have been already proved to be so, and the displacing radicals have been fully recognised; but the bulk of them yet await better processes for the investigation of their molecular constitution. In the present state of our knowledge an alkaloid must be defined as "an organic base analogous to, or derived from, ammonia, and possessing the power of combining with acids to form salts." Like amines, an alkaloid, in combining with an acid, acts as NH_3 would do, and not like the NH_4; *i.e.*, it does not displace the hydrogen, but combines with the whole acid, thus:—

NH_3HCl	$C_{17}H_{19}NO_3HCl$
(Ammonia Hydrochlorate).	(Morphia Hydrochlorate).

III. VOLATILE ALKALOIDS.

CONINE (Conia). Formula, $C_8H_{15}N$.

Is a non-oxygenated substance, which constitutes the active principle of *Conium maculatum*, in which it is usually accompanied by another alkaloid called methylconine, $C_8H_{14}NCH_3$, which is conine having one atom of its hydrogen displaced by methyl.

Impure conine may be prepared by distilling the bruised hemlock seeds with potassium hydrate. The liquid thus obtained contains also a volatile oil and ammonia.

From it the pure conine may be obtained by saturating with dilute sulphuric acid, and shaking with alcohol and ether. The alcoholic ethereal solution is evaporated to dryness, and redistilled with potassium hydrate. Conine is a colourless oily liquid, emitting an odour resembling that of mice. It is lighter than water, having a specific gravity of ·878. It is strongly alkaline to test paper; slightly soluble in water; more so in ether, and very much so in alcohol. It is more soluble in cold than in boiling water. Distilled with oxidizing agents, such as a mixture of sulphuric acid and potassium dichromate, it yields butyric acid:—

$$C_8H_{15}N + O_2 + 2H_2O = 2(C_4H_8O_2) + NH_3.$$

It gives a precipitate with auric chloride, and on the addition of sulphuric acid, evolves great heat, and becomes first red and then greenish. It is also reddened by nitric acid. Two views are at present held as to the constitution of this alkaloid. Judging from the production of butyric acid, as above mentioned, it might be supposed to be NH_3, in which H_2 was replaced by two molecules of the monad radical C_4H_7. M. Werthein has, however, succeeded in isolating a dyad hydrocarbide, which he calls *conylene*, C_8H_{14}, and the composition of conine would therefore appear to be represented by the formula:—

$$N\left\{\begin{matrix}C_8H_{14}\\ H.\end{matrix}\right.$$

Herr Schiff has succeeded in making conine by the action of alcoholic ammonia on butyric aldehyd for two months at 100° F., and then for one day at 212°. By this means a base called dibutyraldine, $C_8H_{17}NO$, is obtained, which by dry distillation yields conine:—

$$C_8H_{17}NO = C_8H_{15}N + H_2O.$$

This artificial conine, which is less soluble in water than the natural alkaloid, and also destitute of action on polarized light, he calls **paraconine**.

(*For detection of Conine, see Author's* **Analytical Chemistry**, *page* 138.)

NICOTINE (Nicotia). Formula, $C_{10}H_{14}N_2$.

This alkaloid, which is the active principle of *Nicotiana Tabacum*, is isolated by exhausting tobacco leaves with water acidulated with hydrochloric acid, concentrating the solution, and distilling with calcium hydrate. The impure nicotine thus obtained may be purified like conine, using calcium instead of potassium hydrate. It is a volatile liquid, very soluble in water, and also in ether. It gives a yellow precipitate with platinic chloride, and a white precipitate with tannic acid. Sulphuric acid produces a port wine colour, which changes to black on heating; chlorine also produces a blood red colour. Nicotine is only present in the merest traces in manufactured tobacco, and not at all in tobacco smoke (*Vohl a. Eulenberg*).

Nicotine may be looked upon as a double molecule of ammonia gas in which the whole of the hydrogen has been displaced by the triad hydrocarbide C_5H_7, thus :—

$$N_2 \begin{cases} C_5H_7. \\ C_5H_7. \end{cases}$$

(*For detection of Nicotine, see Author's* **Analytical Chemistry**, *page* 138.)

CAFFEINE (Theine, *or* Theia). Formula, $C_8H_{10}N_4O_2.H_2O$.

Is a white, crystalline, volatile, alkaloid, which constitutes the active principle of coffee, tea, and guarana, a remedy proposed for headache. Guarana is prepared by the South American Indians from the seeds of the *Paullinia sorbilis*, a climber of the family of the Sapindaceæ. While tea contains but ·06 to 2 per cent. and coffee ·02 to ·08 per cent. of caffeine, guarana contains 4 to 4·28, or occasionally as much as 5 per cent., of that substance. Hence its medical application is intelligible. Theine is prepared by treating an infusion of tea with basic plumbic acetate, which precipitates tannic acid and colouring matter. The solution is then filtered, evaporated to a low bulk, mixed with excess of potassium hydrate, and shaken up with chloroform, which dissolves the theine, and yields crystals on evaporation. Theine may be also prepared by direct sublimation from tea. Treated with strong nitric acid, and then with ammonium hydrate, it produces a reddish-purple colour, and boiled with potassium hydrate, it yields methylamine, recognised by its characteristic odour.

A very simple method of separating and even estimating theine is as follows. The finely powdered tea or coffee is heated with three times its quantity of chloroform. The solution having been poured off and evaporated, the residue is treated with water, and filtered. The filtrate on evaporation leaves a crystalline mass of theine. A cup of coffee or tea from 16 grammes of the former, or 6 grammes of the latter (fine Pekoe), contains about ·1 gramme of caffeine.

SPARTEINE (Sparteia). Formula, $C_{15}H_{26}N$.

Is found in *scoparium*. It is a volatile alkaloid and extremely poisonous. It is not now considered, however, to be the active principle on which the diuretic properties of broom depend. It is sparingly soluble in water, and yields a yellow precipitate with platinic chloride.

It is similar in its action on the system to nicotine, but less energetic.

IV. FIXED ALKALOIDS.

QUININE (Quinia). Formula, $C_{20}H_{24}N_2O_2.3H_2O$. Molecular Weight, 378.

This alkaloid exists in company with cinchonine, quinidine, and other similar bodies, in the bark of the cinchonas. It is chiefly found in the *Cinchona Calisaya*, but it also occurs, though in less quantities, in the *Cinchona succirubra* and *C. lancifolia*. In the *Cinchona Condaminea*, or pale bark, it is rarely present. It is combined in the plant with kinic acid.

It is prepared by precipitating a solution of quinine sulphate with ammonium hydrate, and may be crystallized from strong alcohol. The crystals thus produced are needle-shaped, inodorous, bitter, and fuse at about 300° F., leaving on cooling a yellow resinous-looking mass. Quinine is slightly soluble in water, still more so in alcohol, and freely in ether. Its aqueous solution possesses a faint but decidedly alkaline reaction. It dissolves readily in dilute acids to form salts. It is soluble in excess of ammonium hydrate.

When dissolved in water by the aid of a dilute acid, it forms, on treatment first with chlorine or bromine solution, and subsequently with ammonia, a bright green substance called *thalleiochin*, but if potassium ferrocyanide be added between the two reagents, the colour is an evanescent red. Stannic, mercuric, and platinic chlorides all form insoluble double salts with quinine.

(*For detection of Quinine, see Author's* **Analytical Chemistry**, *page* 138.)

QUININE SULPHATE (SYNS. *Quiniæ Sulphas. Disulphate of Quinine*).
Formula, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O$.

Is prepared by dissolving the alkaloids from cinchona bark by means of maceration and percolation with highly diluted hydrochloric acid; the solution thus obtained containing the quinine, cinchonine, and other principles as hydrochlorates. Excess of sodium hydrate is then added, which precipitates the hydrated alkaloids and forms sodium chloride in solution. The precipitate of the mixed alkaloids, having been washed to remove the colouring matter (cinchona red), is suspended in water, and sufficient diluted sulphuric acid is added to nearly, but not quite, redissolve the precipitate. The object of this is to produce neutral sulphates of the alkaloids, which may be separated by fractional crystallization, the quinine sulphate being much less soluble than that of cinchonine, and therefore crystallizing out first, leaves the latter in solution. It is on this stage of the process that success really depends, as a single drop too much of the sulphuric acid would produce acid sulphates, which could not then be separated by fractional crystallization

Quinine sulphate is in silky, filiform, snow white crystals, slightly soluble in water, yielding a solution which is intensely bitter and highly fluorescent. It is fusible at 240° F., but at a higher temperature it becomes red, and then takes fire and entirely burns away. When exposed to the air it loses water, and when dried at 212° F. it loses 14·44 per cent. of water. As usually met with, it is soluble in 742 parts of cold water, and 80 parts of rectified spirit. It is much more soluble in boiling water, requiring only 30 parts. It is readily soluble in water acidulated with sulphuric acid, as it is then transformed into acid quinine sulphate. It is soluble in 60 parts of cold alcohol, and in 40 of glycerin, as well as freely in creasote; but it has been stated not to be soluble in fatty oils. It is also readily soluble in aqueous or spirituous solutions containing excess of ammonium hydrate. A solution of quinine sulphate mixed with an alcoholic solution of iodine, lets fall a brilliant green compound called *Herapathite*, which is constant in composition, and has the formula $(C_{20}H_{24}N_2O_2)_2\,3H_2SO_4\,I_6 + 3H_2O$. It has optical properties similar to tourmaline, and when dried at 212° F., one part of it represents ·565 parts of quinine.

(*For detection of adulterants in Quinine Sulphate, see Author's* **Analytical Chemistry**, *page* 139.)

QUININE HYDROGEN-SULPHATE. Formula, $C_{20}H_{24}N_2O_2.H_2SO_4.7H_2O$.

Is produced when quinine sulphate is dissolved in dilute sulphuric acid. Its solution appears blue when held up to the light, and it thus possesses in a marked degree the curious property of *fluorescence*, *i.e.*, the altering of the refrangibility of the invisible chemical rays of light, so as to render them visible. It also turns the plane of polarization of light to the right.

QUININE HYDROCHLORATE (SYN. *Muriate of Quinine*).
Formula, $C_{20}H_{24}N_2O_2.HCl.3H_2O$.

Is produced when quinine is dissolved in dilute hydrochloric acid, avoiding excess.

QUININE HYPOPHOSPHITE. **Formula, $C_{20}H_{24}N_2O_2.HPH_2O_2$.**

Prepared by dissolving quinine sulphate in water by the aid of hypophosphorous acid, and then adding baric hypophosphite, carefully avoiding excess.

$$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + Ba2PH_2O_2 = 2(C_{20}H_{24}N_2O_2.HPH_2O_2) + BaSO_4.$$

It is soluble in 60 parts of water, and is a light mass, with a bitter taste, readily fusible, and turning brown on heating.

QUININE PHOSPHATE. **Formula, $(C_{20}H_{24}N_2O_2)_2.H_3PO_4.2H_2O$.**

Prepared by precipitating quinine from the sulphate by ammonium hydrate, and dissolving the precipitate in phosphoric acid. It forms a white silky crystalline mass, very slightly soluble in water. The substance sold under this name is commonly prepared by simply adding sodium phosphate to solution of quinine sulphate, and separating and drying the white substance which deposits.

QUININE LACTATE.

Prepared by dissolving quinine in lactic acid. Has been introduced into use in medicine; as also the **valerianate**, which is prepared from quinine sulphate and alkaline sodium valerianate.

CINCHONINE (Cinchonia). **Formula, $C_{20}H_{24}N_2O$.**

This alkaloid is a constituent of most cinchona barks, but according to Mr. Howard, the proportion in the *C. Condaminea* is, contrary to the received idea, usually only slight. It may be isolated from its salts by precipitating with ammonium hydrate, and then crystallizing from alcohol, in which it is somewhat soluble. It is practically insoluble in water and also in ether, which latter property serves as a marked distinction from quinine. Cinchonine when heated to 430° F. partly sublimes. It is not precipitable in the cold by sodium hydrogen-carbonate in the presence of tartaric acid, but heating the liquid causes precipitation, accompanied by evolution of carbonic anhydride.

It is not soluble in excess of ammonium hydrate.

(*For detection of Cinchonine, see Author's* **Analytical Chemistry**, *page* 139.)

CINCHONINE SULPHATE. **Formula, $(C_{20}H_{24}N_2O)_2.H_2SO_4.2H_2O$.**

Is crystallized from the liquors poured off from the crystals of quinine disulphate after the B.P. process. It crystallizes in prisms, short and broken, and is much more soluble in water and alcohol than the quinine salt, but totally insoluble in ether. Its solution is not fluorescent.

CINCHONINE HYDROGEN-SULPHATE.

Is produced, like the quinine salt, by excess of sulphuric acid.

CINCHONINE HYDROCHLORATE (SYN. *Muriate of Cinchonia*). **Formula, $C_{20}H_{24}N_2O.HCl.2H_2O$.**

Is also employed in medicine, and of late years has been strongly recommended. It is much more soluble in water than the sulphate, and even slightly so in ether.

Two muriates were mentioned in the original memoir of Pelletier and Caventou.

Dimuriate of Cinchonia		Muriate of Cinchonia	
Cinchonia . . .	89·5	Cinchonia . .	81·0
Acid. Muriat. . .	10·5	Acid. Muriat. . .	19·0
	100·0		100·0

The hydrochlorates of cinchonine and cinchonidine present this curious phenomenon: these salts dissolve indeed instantly in the chloroform; but the solution, after a short time, and at the original temperature, becomes thick and crystalline, owing to the formation of difficultly soluble compounds of the salts with the solvent.

In such compounds, 1 part of cinchonidine hydrochlorate requires 13 parts of pure chloroform at 20° C., and 1 part of cinchonine hydrochlorate requires 22·2 parts of pure chloroform at 15° C., for solution. On evaporation of the solution the cinchonine hydrochlorate remains behind as an amorphous resinous mass, which, without increase of weight, gradually changes into radiating crystals. It is the anhydrous substance $C_{20}H_{24}N_2O\,HCl$. The different behaviour of quinine sulphate and cinchonine hydrochlorate with pure chloroform furnishes a ready and convenient method of detecting the latter salt when mixed with the former.—*O. Hesse.*

QUINIDINE (Quinidia). Formula, $C_{20}H_{24}N_2O_2$.

Is a modification of quinine, found chiefly in the pale and Carthagena barks, which agrees with quinine in bitterness, fluorescence of its salts, and in general reactions. It may be separated from quinine by dissolving in the smallest possible excess of acetic acid and adding strong solution of potassium iodide, which forms an insoluble precipitate of quinidia hydriodide. Quinidia is soluble in ether, from which it crystallizes in long prisms.

CINCHONIDIA. Formula, $C_{20}H_{24}N_2O$.

This alkaloid is insoluble in ether, but crystallizes from alcohol in anhydrous, rhombic prisms. It is isomeric with cinchonia, from which it may be separated by precipitation of the mixed sulphates by Rochelle salt, when it is precipitated as tartrate, leaving the cinchonia in solution.

Quinicine and **Cinchonicine** are amorphous alkaloids, produced in the making of the quinine. They are not crystallizable, and are doubtless formed by the action of the mineral acids; possessing about the same relation to quinine and cinchonine, as treacle and sugar bear to each other. They are sometimes classed together under the name of quinoidine, and are extracted from a quinine residue by alcohol of 40 per cent., in which they dissolve.

QUINAMINE. Formula, $C_{19}H_{24}N_2O_2$.

Is an alkaloid found in certain Indian varieties of *Cinchona succirubra.* It is obtained mixed with the amorphous alkaloids, and may be separated by dissolving the mass and adding potassium thiocyanate, when the quinamine escapes precipitation and may then be extracted by shaking with ether in the presence of excess of ammonium hydrate. It is crystalline, soluble in dilute alcohol, and *dextro-rotary.*

Alkaloids of Opium.

These alkaloids exist in combination with meconic acid. The chief ones are as follows :—

Morphine (Morphia)	$C_{17}H_{19}NO_3$.
Codeine (Codeia)	$C_{18}H_{21}NO_3$.
Narcotine (Narcotia, Anarcotine)	$C_{22}H_{23}NO_7$.
Narceine (Narceia)	$C_{23}H_{29}NO_9$.
Thebaine (Paramorphine)	$C_{19}H_{21}NO_3$.
Meconine	$C_{10}H_{10}O_4$.

MORPHINE (Morphia). Formula, $C_{17}H_{19}NO_3.H_2O$. Molecular Weight, 303.

Is prepared, according to the B.P., by extracting the soluble portion of opium by three macerations with water. This process extracts the morphine and codeine as meconates, together with a small portion of the other alkaloids. The chief part of the narcotine remains in the insoluble portion of the opium. The solution thus obtained is then treated with calcium chloride, which forms calcium meconate and morphine and codeine hydrochlorate. The calcium meconate not being entirely insoluble in water, and more especially when the opium solution is slightly acid, cannot be at once removed by filtration, and therefore the whole solution is evaporated until it crystallizes, and the crystalline mass is subjected to strong pressure to remove the dark-coloured mother-liquors. The pressed cake, which contains calcium meconate and undecomposed chloride, together with morphine and codeine hydrochlorates, is then treated with boiling water, which dissolves the latter substances, leaving the insoluble calcium meconate, which is filtered out. The solution is again evaporated, crystallized, the cake again pressed and submitted to the action of boiling water; this process is repeated three times in all, to ensure a thorough separation of the calcium meconate and colouring matters. The purified cake is dissolved in boiling water, and digested with animal charcoal, to remove the last traces of colouring matter. A solution is thus obtained which contains tolerably pure hydrochlorates of morphine and codeine. Ammonium hydrate is added in very slight excess, which precipitates most of the morphine, while the codeine remains dissolved by the slight excess of the ammonium hydrate. The precipitate is filtered out and washed. It may be made into any salt desired, by using an appropriate acid. This process will be found detailed in the words of the B.P. under *morphia hydrochlorate.*

As thus prepared, morphine presents itself as a crystalline mass, with an alkaline reaction and bitter taste.

It is practically insoluble in water and ether, but is soluble in sodium or potassium hydrate, hence it cannot be precipitated from its solution by these reagents. It is also soluble in a good excess of ammonium hydrate. These reactions serve to distinguish it from quinine, cinchonine, strychnine, and most other alkaloids, which are not soluble in excess of potassium or sodium hydrate. It is precipitated from its solution by sodium carbonate.

Morphine gives an orange-red solution in strong nitric acid; but its solution in strong sulphuric acid has no colour unless nitric acid be also present.

It also possesses the power of liberating iodine from iodic acid.

(*For detection of Morphine, and its estimation in opium, see Author's* **Analytical Chemistry**, *pages* 139, 143, 192.)

MORPHINE HYDROCHLORATE (SYNS. *Morphiæ Hydrochloras. Muriate of Morphia*) **Formula, $C_{17}H_{19}NO_3HCl.3H_2O$.**

Is prepared by diffusing pure morphia, obtained as above, through two fluid ounces of boiling distilled water placed in a porcelain capsule kept hot, and adding (constantly stirring) diluted hydrochloric acid, proceeding with caution, so that the morphia may be entirely dissolved, and a neutral solution obtained. Set aside to cool and crystallize. Drain the crystals, and dry them on filtering paper. Thus prepared, it is in white fusible acicular prisms of a silky lustre, not changed by exposure to the air, soluble in water and spirit.

MORPHINE ACETATE (SYN. *Morphiæ Acetas*). **Formula, $C_{17}H_{19}NO_3C_2H_4O_2$**

Is prepared by dissolving hydrochlorate of morphia in one pint of distilled water, and carefully adding ammonium hydrate until the morphia is precipitated and the liquid rendered slightly alkaline. Collect the precipitate on a filter, wash it with distilled water, then, having transferred it to a porcelain dish, add four ounces of distilled water and a sufficient quantity of acetic acid to neutralize and dissolve it. Evaporate the solution by the heat of a water bath until it concretes on cooling. Lastly, dry the salt with a gentle heat, and reduce it to powder. Thus made, it is a white powder, soluble in water and in spirit (not so soluble in the latter as in the former).

On evaporating, its solution decomposes, depositing morphine and evolving acetic acid.

Morphine also forms sulphates, phosphates, and many other salts. The morphine sulphate is much more soluble than has been generally supposed.

APOMORPHINE (Apomorphia). Formula, $C_{17}H_{17}NO_2$. [*Matthiessen & Wright.*]

This very active alkaloid is prepared artificially by hermetically sealing a mixture of morphine hydrochlorate with excess of hydrochloric acid in a strong glass tube, and heating for some hours to 300° F. in an oil bath. The tube having been broken and water added to its contents, the solution is treated with sodium hydrogen carbonate, which precipitates the alkaloid. Its hydrochlorate contains no water of crystallization and agrees with the formula $C_{17}H_{17}NO_2HCl$; it is prepared by dissolving the precipitate in chloroform, and shaking the solution with a little hydrochloric acid, when the salt crystallizes out. This base, as its formula indicates, is simply produced from morphine by the removal of a molecule of water on heating with a strong acid.

$$C_{17}H_{19}NO_3 - H_2O = C_{17}H_{17}NO_2.$$

The physiological effects of apomorphine are not only remarkable in themselves, but totally distinct from those of morphine, although these substances differ so slightly in chemical constitution. When subcutaneously injected, one tenth of a grain produces vomiting in less than ten minutes.

CODEINE (Codeia). Formula, $C_{18}H_{21}NO_3$.

May be prepared from the solution filtered from the precipitate of morphine in the B P process, by precipitation with dilute potassium hydrate. It is white and crystalline; is soluble in water, alcohol, and ether. Its solution has an alkaline reaction, which serves to distinguish it from meconine. It is distinguished from morphine by its not dissolving in potassium hydrate, and not giving a blue colour with ferric chloride. When treated in a sealed tube

with hydrochloric acid, it loses water and yields apomorphine, producing at the same time methyl chloride :—

$$C_{18}H_{21}NO_3 + HCl = C_{17}H_{17}NO_2 + H_2O + CH_3Cl.$$

From this reaction we may draw the conclusion that codeine differs from morphine only in having the organic radical methyl as a constituent of its molecule. It has, therefore, been proposed to call it methyl-morphine.

(*For detection of Codeine, see Author's* **Analytical Chemistry**, *page* 140.)

NARCOTINE (Narcotia). (SYN. *Anarcotine* [*Squire*].) **Formula, $C_{22}H_{23}NO_7$**

Narcotine has been shown to have no soporific influence either on men or animals, hence the new synonym proposed. These experiments have been confirmed by Flückiger. It is prepared from the insoluble portion of opium by heating with dilute acetic acid, which extracts the alkaloid as acetate ; and then precipitating wtih ammonium hydrate, and purifying by crystallization from boiling alcohol. It is a white crystalline substance, insoluble in cold water, but soluble in alcohol, also in ether.

It is distinguished from morphine by not giving a blue colour with ferric chloride, nor decomposing iodic acid. When heated on paper, it causes a greasy stain. It may be extracted from Persian opium, together with oil, etc., by percolation with petroleum spirit.

(*For detection of Narcotine, see Author's* **Analytical Chemistry**, *page* 140.)

NARCEINE (Narceia). Formula, $C_{23}H_{29}NO_9$.

Crystallizes in silky needles, with a bitter taste. It is soluble in water, and when treated with dilute nitric acid strikes a light blue colour. It also forms with iodine a blue iodide, and is thus easily distinguished from all other alkaloids.

(*For detection of Narceine, see Author's* **Analytical Chemistry**, *page* 140.)

THEBAINE (Thebaia). Formula, $C_{19}H_{21}NO_3$.

Is a white crystalline solid, with an inky taste, scarcely soluble in water, but easily in alcohol and ether. It is not soluble in excess of sodium hydrate, and although soluble in acids, it refuses to form crystalline salts. This serves to distinguish it from both morphine and codeine, while, from the former, it still further differs by not giving a blue colour with ferric chloride.

(*For detection of Thebaine, see Author's* **Analytical Chemistry**, *page* 141.)

MECONINE (Meconia). Formula, $C_{10}H_{10}O_4$.

This differs from all the other opium alkaloids in not containing nitrogen, and therefore not evolving ammonia when heated with soda-lime.

It is further distinguished by being very readily fusible, and not possessing alkaline reaction.

(*For detection of Meconine, see Author's* **Analytical Chemistry**, *page* 140.)

In addition to the above, the following rarer alkaloids have been discovered in opium by various chemists :—

Codamine	$C_{20}H_{25}NO_4$.	Meconidine	$C_{21}H_{23}NO_4$.
Cryptopia	$C_{21}H_{23}NO_5$.	Opianine	$_{21}H_{21}NO_7$.
Hydrocotarnine	$C_{12}H_{15}NO_3$.	Papaverine	$C_{21}H_{21}NO_4$.
Lanthopine	$C_{23}H_{25}NO_4$.	Protopine	$C_{20}H_{19}NO_5$.
Laudanine	$C_{20}H_{25}NO_4$.	Pseudomorphia	$C_{17}H_{19}NO_4$.
Laudanosine	$C_{21}H_{27}NO_4$.	Rhæadine	$C_{20}H_{21}NO_6$.

The Alkaloids of Nux Vomica are :—

Strychnine (Strychnia)	$C_{21}H_{22}N_2O_2$.
Brucine (Brucia)	$C_{23}H_{26}N_2O_4$.

They are both found in the *Strychnos Nux vomica* and in the *Ignatia amara*, besides several other plants of the same sub-order, combined with igasuric acid.

STRYCHNINE (Strychnia). Formula, $C_{21}H_{22}N_2O_2$. Molecular Weight, 334.

Is prepared by powdering the beans, and exhausting them with dilute alcohol. After removing the spirit by distillation, there remains a watery solution containing the alkaloids as igasurates. To this solution plumbic acetate is added, which forms a precipitate of igasurate of lead and resinous matters, leaving the alkaloids in solution as acetates. After concentration, a slight excess of ammonium hydrate is added, which precipitates the impure alkaloids, which are filtered out, washed, and dried.

Thus we have a pulverulent mass, consisting of strychnine and brucine, together with certain impurities. This mass is exhausted with successive portions of boiling rectified spirit; the point of exhaustion being known by the alcohol ceasing to taste bitter. The bulk of the spirituous solution of pure strychnine and brucine thus obtained having been reduced by distillation, the residue is finally evaporated to a small bulk, and set aside to crystallize. The strychnine, being much less soluble than the brucine, crystallizes out, leaving the latter in solution, and the crystalline crust is once more dissolved in spirit and recrystallized.

Thus made, strychnine is in right square octahedra, or prisms, colourless and inodorous; sparingly soluble in water, but communicating to it its intensely bitter taste; soluble in boiling rectified spirit and in chloroform, but not in absolute alcohol or in ether. Pure sulphuric acid forms with it a colourless solution, which on addition of potassium dichromate acquires an intensely violet hue, speedily passing through red to yellow. Not coloured by nitric acid; leaves no ash when burned with free access of air.

A very active poison. Strychnine has an alkaline reaction, and forms salts with acids. It has also a great tendency to produce double salts when added to solutions of salts of heavy metals. For example, mercuric chloride with strychnine hydrochlorate, produces strychnine chloromercurate, which takes the form of a white gelatinous precipitate, $C_{21}H_{22}N_2O_2.HCl.HgCl_2$.

(*For detection of Strychnine, see Author's* **Analytical Chemistry**, *page* 141.)

The bitter of strychnine is so intense that it is easily perceivable in a solution containing [illegible] of its weight of the alkaloid. According to Pelletier, it is soluble in 6667 parts of cold, and 2500 parts of boiling water. Salts of strychnine may be prepared by dissolving the alkaloid in almost any acid, the chief commercial ones being the following:—

Hydrochlorate	$C_{21}H_{22}N_2O_2.HCl$.
Sulphate	$2(C_{21}H_{22}N_2O_2).H_2SO_4$.
Acid Sulphate	$C_{21}H_{22}N_2O_2.H_2SO_4$.

The salts are precipitated by tannic acid, but are not affected by gallic acid or by ferric salts. On treatment with ammonium hydrate or any alkaline hydrate, pure strychnine is precipitated.

BRUCINE (**Brucia**). **Formula,** $C_{23}H_{26}N_2O_4$.

Is crystallized from the mother-liquid poured off from the crust of strychnine in the B.P. process. It is a white crystalline substance, sometimes in prisms, and at others in laminæ. It has a less intense bitter taste than strychnine, and is much more soluble, both in water and alcohol, one part requiring only 850 of cold and 500 of boiling water. It forms salts with most acids, which, however, are not of sufficient interest to require detailed notice. The solution of brucine in strong nitric acid is blood-red, but becomes yellowish on heating; and the addition of stannous chloride causes a violet colour. Brucia also forms an orange insoluble compound with potassium iodide.

(*For detection of Brucine, see Author's* **Analytical Chemistry**, *page* 141.)

The remaining alkaloids which are official in the B.P. are :—

Atropine (Atropia)	$C_{17}H_{23}NO_3$.
Beberine (Beberia)	$C_{19}H_{21}NO_3$.
Aconitine (Aconitia)	$C_{30}H_{47}NO_7$.
Veratrine (Veratria)	$C_{32}H_{52}N_2O_8$.

ATROPINE (**Atropia**). **Formula,** $C_{17}H_{23}NO_3$.

Is found in *Atropa Belladonna*, in which it exists as atropine malate. It is prepared by exhausting belladonna root with spirit, and shaking the spirituous solution with calcium hydrate, which precipitates the malic acid and colouring matter. These are removed by filtration, and sulphuric acid is added to the filtrate to form sulphate of atropine, so as to prevent the decomposition which the alkaloid undergoes when heated with alkalies in the free state. After concentration a little potassium carbonate is added, so as nearly, but not quite, to neutralize the acid. This causes a further separation of resinous matter, which is removed by filtration; excess of potassium carbonate is added, which precipitates the atropine, and the mixture is immediately shaken up with chloroform, which dissolves the alkaloid.

The chloroform having been distilled off, the residue is further purified by solution in spirit, decolorization with animal charcoal, and crystallization. The yield by this process is very small, two pounds of the root rarely producing more than forty grains of the alkaloid.

Thus prepared, atropine is in colourless, acicular crystals, sparingly soluble in water, more readily in alcohol and in ether. Its solution in water has an alkaline reaction, gives a citron-yellow precipitate with auric chloride, has a bitter taste, and powerfully dilates the pupil of the eye when administered internally. Physically, therefore, it has a diametrically opposite action to physostigmine, which powerfully contracts the pupil. Advantage is taken of the distinctive action existing between these two alkaloids in ophthalmic practice.

It leaves no ash when burnt with free access of air. It is an active poison. Atropine is fusible, and partly volatile by heat. When boiled with potassium hydrate, it evolves ammonia.

Tincture of iodine reddens a solution of its salts, which also give a precipitate with tannic acid and platinic chloride. By heating with strong sulphuric acid it turns brown; and on the addition of a little water, a powerful odour of orange flowers is evolved.

(*For detection of Atropine, see Author's* **Analytical Chemistry**, *page* 141.)

Atropine forms salts with most acids, such as the hydrochlorate, acetate, and sulphate. The latter is alone official in the B.P. for the purposes of ***external application*** only.

It is a colourless powder, soluble in water, forming a solution which is neutral to test-paper, and which when applied to the eye dilates the pupil in a similar manner to the solution of atropine. It leaves no ash when burned with free access of air.

BEBERINE (Beberia). **Formula, $C_{19}H_{21}NO_3$.**

Is formed in the bark of the *Nectandra Rodiæi*, together with tannic and beberic acids. It is a yellow substance of a resinous appearance, decidedly alkaline, and only slightly soluble in water, more so in ether, and easily in alcohol. It is prepared by precipitating its sulphate with ammonium hydrate, mixing the precipitate with plumbic hydrate (to remove traces of tannic acid), evaporating the whole to dryness, and purifying by successive solution, first in alcohol and then in ether. It is soluble in acids, forming a yellow solution, and yielding on evaporation salts which are not crystallizable. When heated with sulphuric acid or potassium acid chromate, it forms a black resinous mass. A curious characteristic is, that by friction with a piece of silk, it becomes electrical, and will affect a galvanometer, and attract very small pieces of light paper.

(*For detection of Beberine, see Author's* **Analytical Chemistry**, *page* 142.)

BEBERINE SULPHATE (Syn. *Beberiæ Sulphas*).

Formula, $2(C_{19}H_{21}NO_3).H_2SO_4$. B.P. Formula, $C_{38}H_{42}N_2O_6.H_2SO_4$.

Is prepared, in a not exactly pure condition, by exhausting the bark with very dilute sulphuric acid, and nearly neutralizing with lime, filtering, and precipitating with ammonium hydrate. This yields the alkaloid. The precipitate is dissolved in alcohol, filtered, and the spirit is distilled off. Sulphuric acid having been added, the whole is evaporated to dryness. The residue, containing impure beberine sulphate, is extracted with water; the solution thus obtained, not being crystallizable, is evaporated and scaled at a heat not exceeding 140° Fahr. Thus made, it is in dark-brown, thin, translucent scales, yellow when in powder, with a strong bitter taste, soluble in water and alcohol.

Beberine must not be confused with berberine, also a yellow alkaloid, found in calumba root, the *Hydrastis Canadensis*, and in podophyllum.

ACONITINE (Aconitia). **Formula, $C_{30}H_{47}NO_7$.**

An alkaloid obtained from the leaves and root of *Aconitum Napellus*.

It is a light, pulverulent substance, usually,—in the most highly prized commercial specimens,—occurring in irregular, small, flattened pieces. Soluble in acids, without, however, producing crystallizable salts. As usually prepared, it is in a hydrated condition, and contains 20 per cent. of water, which passes off at about 168° F.

With tincture of iodine, it forms an orange-coloured precipitate.

Nitric acid has no effect on aconitine; but strong sulphuric acid produces first a yellow and then a violet colour, and syrupy phosphoric acid also colours it violet. In common with most alkaloids it is precipitable by auric chloride, platinic chloride being devoid of action. It is prepared by exhausting aconite root with spirit, which dissolves the natural aconitate of aconitine.

The alcohol having been distilled off, the residue is dissolved in water, which causes the separation of resinous matters. The solution is then precipitated by ammonia, which separates the alkaloid in an impure condition. This precipitate is dried, powdered, and exhausted with ether, which dissolves only the aconitine. The ether having been distilled off, the residue is treated with dilute sulphuric acid, and the alkaloid, having thus been obtained in solution as sulphate, is once more precipitated with ammonia, this time in a pure condition.

[illegible]

[illegible] **Analytical Chemistry**, [illegible]

VERATRINE [illegible] **Formula** [illegible]

[illegible]

[illegible] **Analytical Chemistry**, [illegible]

[illegible] considered to be the active principle of the *C*[illegible] [illegible] been found to be an alkaloid which has been [illegible]. It differs from veratrine in being crystallizable, soluble in [illegible]. Concentrated sulphuric acid causes a play of [illegible] commencing with violet and passing through blue and green. [illegible]

Unguentum Veratriæ (eight grains to an ounce of lard) is official.

JERVINE (**Jervia**). **C**[illegible]**H**[illegible]**N**[illegible]**O**[illegible].

[illegible] exists in the roots of *Veratrum album* and of *V. viride*, from a [illegible] of which it may be prepared by precipitating resinous [illegible] acetic acid and water, filtering, and precipitating the impure alkaloid by sodium carbonate in large excess. The precipitate is then dried, [illegible] with boiling alcohol, the solution evaporated to dryness, and the [illegible] digested in hot and very dilute sulphuric acid. On cooling, granules of [illegible] separate out, from which the pure alkaloid may be prepared by boiling with sodium carbonate.

Thus prepared, jervine is a granular powder, soluble in alcohol, from which it crystallizes in small prisms. When a fragment of this alkaloid is moistened with strong sulphuric acid, it becomes first straw-yellow, and then gradually dark green.

DELPHININE (**Delphinia**). **Formula**, $C_{24}H_{35}NO_2$.

Exists in the seeds of the *Delphinium Staphisagria*.

HYOSCYAMINE (**Hyoscyamia**). **Formula,** $C_{18}H_{23}N_2O_3$.

Exists in the seeds of *Hyosciamus niger*.

EMETINE (**Emetia**). **Formula,** $C_{30}H_{44}N_2O_8$.

This alkaloid is a white pulverulent mass obtained from and being the active principle of *Cephælis Ipecacuanha*. It is only slightly soluble in water, but very easily so in alcohol.

(*For estimation of Emetine in Ipecacuanha, see Author's* **Analytical Chemistry**, *page* 193.)

The chief remaining fixed alkaloids are as follows:—

Name.	Formula.	Source.
Berberine	$C_{20}H_{17}NO_4$ . . .	*Calumba root.*
Cissampeline . .	$C_{18}H_{21}NO_3$ . . .	*Cissampelos Pareira.*
Physostigmine . .	Undetermined . .	*Calabar Bean.*
Solanine	$C_{43}H_{70}NO_{16}$ . . .	*Solanum dulcamara.*
Piperine	$C_{17}H_{19}NO_3$ . . .	*Pepper.*

These and many other non-official alkaloids will be found fully described in the **Author's work** on **Organic Materia Medica**, to which the student is referred.

V. NITRILS.

Are derived from ammonia by the entire displacement of its hydrogen by a triad basylous radical. Each nitril is isomeric, and identical with the cyanide of the monad radical immediately below in carbon value, as already seen (page 210).

ETHENYL NITRIL (Syns. *Acetonitril. Methyl Cyanide*).
Formula, $N'''.C_2H_3$, or $CH_3'''.CN$.

Is an oily liquid, having (when pure) a fragrant odour, and boiling at 170° F., which is prepared

1. By the dehydrating action of phosphoric anhydride on ammonium acetate:—

$$(NH_4)C_2H_3O_2 - 2H_2O = N.C_2H_3.$$

2. By distilling potassium cyanide with potassium methyl sulphate:—

$$KCN + K.CH_3SO_4 = N.C_2H_3 + K_2SO_4.$$

All the other nitrils are similar to this, rising in a regular series of boiling points, and prepared by similar processes. They are employed to convert an alcohol into the acid immediately above it in carbon value, because, when heated with potassium hydrate, they take up water and yield ammonia and the corresponding acid. Thus, amyl cyanide, prepared from amyl alcohol, is capronitril, and when heated with KHO it yields ammonia and caproic acid. Certain modified nitrils have been discovered, which are not readily affected by alkalies, but when treated with dilute acids yield formic acid, and the corresponding **amine**. They are called **isocyanides**, or **carbamines**, and are prepared by heating an amine with chloroform in the presence of alcoholic potash to neutralize the HCl set free. They have a very peculiar and disgusting odour, which is utilized as a test for the presence of chloroform by heating the suspected liquid with aniline and alcoholic potash, so producing phenyl isocyanide.

$$C_6H_7N + CHCl_3 = N.C_7H_5 + 3HCl.$$

CHAPTER XX.

THE GLUCOSIDES.

THESE bodies have for the most part very complicated formulæ, and consequently their composition cannot be regarded as having been, in all cases, determined with exactitude. The quality from which they derive their name is that of yielding glucose when boiled with water and a dilute acid. This reaction invariably results in the production of one or more compounds characteristic in their nature of the special glucoside taken for the experiment, and consists of the assimilation of the elements of water, accompanied by molecular disruption.

The term *saccharogens*, *glucosamides*, and sometimes *saccharides*, have also been applied to glucosides.

AMYGDALIN. Formula, $C_{20}H_{27}NO_{11}$.

This glucoside is contained in the cherry-laurel and in bitter almonds.

It exists in the latter to the extent of nearly two per cent., but is not a constituent of sweet almonds.

Amygdalin is usually prepared from bitter almonds by reducing them to a paste, extracting the fixed oil by pressure, exhausting the residue by boiling alcohol, precipitating by ether and purifying the result by pressure between blotting paper, and washing with ether. Thus procured, it is in opalescent laminæ, which have the formula $C_{20}H_{27}NO_{11}.3H_2O$. Anhydrous amygdalin is an inodorous solid which is insoluble in ether. It does not dissolve in cold water very freely, but is more soluble in warm water. Upon the palate it produces an impression which at first is pleasant, but soon becomes disagreeably bitter. When in solution the former effect does not result, only a faint bitterness being perceptible, on account of the limited degree of its solubility in water at 60° F.

By contact with a ferment known as *emulsin* or *synaptase*, glucose, benzoic aldehyd, and hydrocyanic acid result, thus :—

$$C_{20}H_{27}NO_{11} + 2H_2O = 2C_6H_{12}O_6 + C_7H_6O + HCN.$$

In theory, 457 of the anhydrous variety should yield 27 of hydrocyanic acid; but practically to produce 1 of the acid it is necessary to employ 17 of amygdalin. It is by no means unlikely that this process may in the course of time be employed for the preparation of hydrocyanic acid for medicinal purposes. Independently of the ascertained and undoubted characters of amygdalin as a glucoside, its behaviour under the influence of alkaline hydrates indicates conclusively that it may be regarded as amygdalamide. The reasons for declaring this to be the true composition arise from amygdalin yielding, like amides generally, ammonia gas (NH_3) when boiled with sodium hydrate; the bye-product being sodium amygdalate, from which a strong acid

liberates amygdalic acid. As a necessary consequence of its being decomposed by both acids and alkaline hydrates, amygdalin does not form a combination with either.

Aqua laurocerasi, B.P., contains an analogous body to amygdalin, with which it is possibly identical. By a decomposition varying little if at all from that in the case of almonds, the same products result. The amount of the glucoside present, however, does not appear to be so fixed as to render the percentage of hydrocyanic acid formed by the action of the ferment which accompanies it, variable within anything like definite limits, and thus this pharmacopœial preparation is both useless and dangerous to employ medicinally.

CATHARTIC ACID. Formula, $C_{180}H_{192}N_4SO_{82}$.

The above formula is that deduced by the discoverers of this body, which is the purgative principle of Indian and Alexandrian *senna* (*Senna Indica* and *Senna Alexandrina*, B.P.). It is, however, exceedingly doubtful whether the numbers involved are so high as above represented, though the readiness of decomposition indicates an excessively complex molecular constitution. It is only soluble in water when in the form of a metallic salt, in which condition it is found in the plants above mentioned. It is not dissolved by alcohol and ether, but boiling with potassium hydrate causes speedy dissolution of the molecule. The glucosic body derived by the action of dilute sulphuric acid is of a special nature, and the principle simultaneously formed does not greatly differ in its molecular weight from cathartic acid itself, being $C_{132}H_{116}N_4SO_{44}$, and bearing the name of *cathartogenic acid*. The reaction by which cathartic acid splits up cannot in the present state of our knowledge be very well traced.

The **magnesium salt** is that which exists in solution in "black draught" (*infusum sennæ co.*, B.P.), being formed by the action of the magnesium sulphate on the natural cathartate.

Ammonium cathartate may be procured by dissolving the acid in ammonium hydrate; and, as it is a well-defined salt which may be obtained in the solid state, it is very suitable for preparing other cathartates. No decomposition occurs when it is brought into an antimonious solution; when it comes in contact with tannin; nor when presented to the ferrocyanic and ferricyanic salts of potassium. The argentic, stannous, stannic, cupric, mercuric, and plumbic salts are insoluble and of a neutral tint.

The manner of isolating the natural cathartate in senna usually given, is by acting on an aqueous infusion, after evaporating as much as possible under the air pump, with alcohol of 90 per cent., or more. This throws down some of the cathartate, but a still larger quantity is precipitated when absolute alcohol is added to the filtrate. It has been found that the first precipitate is much contaminated with colouring matter, and hence the second alone is submitted to purification. All that is required is to subject it to a series of successive solutions in water, and separation by alcohol. When the resulting pure salt is dialyzed (with hydrochloric acid) through a parchment septum, the metallic chloride alone passes through, together with the excess of acid. There are some reasons to believe that the purgation caused by the use of buckthorn juice (*rhamni succus*, B.P.), arises from its containing cathartic acid or an analogue.

ARBUTIN. Formula, $C_{12}H_{16}O_7$.

Is believed to be one of the active ingredients of bearberry leaves (*Arctostaphylos uva ursi*).

When pure, it is crystalline, has a bitter taste, and is soluble in ether, alcohol, and water. By boiling with a dilute acid it gives birth to hydro-quinone and glucose :—

$$C_{12}H_{16}O_7 + H_2O = \underset{\text{(Hydroquinone.)}}{C_6H_6O_2} + C_6H_{12}O_6.$$

The same transformation ensues by the action of emulsin. It differs from most similar bodies by not forming any precipitate with either plumbic oxy-acetate, plumbic acetate, or ferric chloride. A mixture of manganic dioxide and sulphuric acid produces formic acid and quinone when allowed to act upon arbutin.

SALICIN. Formula, $C_{13}H_{18}O_7$.

Derives its name from the willow-tree (*Salix*), in the bark of which it is contained abundantly. Other of its sources are castor (*castoreum*, B.P.) and the bark of the poplar.

Salicin is extracted by digesting willow bark with water and plumbic oxide in fine powder for a day, and then filtering and evaporating the filtrate to a low bulk. The crystalline mass which separates out on cooling, frequently possesses a yellow colour, but this may be destroyed by digestion with animal charcoal. When pure, it is composed of small, opaque, scaly, white crystals, which are not dissolved by ether, and are more readily soluble in water than in alcohol. It is neutral to test-paper, and does not decompose under 390° F., and requires a very strong heat to completely destroy it. Gelatin, plumbic acetate, or plumbic oxyacetate, added to a solution of salicin, form no precipitates; but when strong sulphuric acid is dropped upon solid salicin, a deep red coloration is produced, which is due to the formation of an acid analogous to sulphindigotic or phenyl-sulphuric acid is the result. On heating with a dilute acid, salicin is converted into glucose and *saligenin*, thus :—

$$C_{13}H_{18}O_7 + H_2O = C_6H_{12}O_6 + \underset{\text{(Saligenin.)}}{C_7H_8O_2}.$$

The best way of causing the reaction is to heat the salicin with solution of benzoic acid in a sealed tube. The resulting liquid may be proved to contain glucose by boiling with *Fehling's solution* and saligenin by turning blue with ferric chloride. Distillation with oxidizing mixtures, such as potassium dichromate and sulphuric acid, decomposes salicin with the formation of **salicylol** (*salicosyl hydride*, or *salicylous acid*, $C_7H_6O_2$). This is the substance which consitutes the peculiar odoriferous principle of various species of *Spiræa* (meadow-sweet), heliotrope, and of some beetles. The sulphuric acid appears to ensure the production of saligenin, which oxygen afterwards converts into salicylol. Thus :—

$$2C_7H_8O_2 + O_2 = \underset{\text{(Salicylol.)}}{2C_7H_6O_2} + 2H_2O.$$

The condensed salicylol forms a purplish solution (not greatly differing from that produced by saligenin) upon subjection to the action of ferric chloride. It forms two classes of compounds, one rendering it analogous to aldehyds, the other indicating a resemblance to acids. By oxidation it yields salicylic acid.

CROCIN. Formula, $C_{16}H_{18}O_6$.

Is contained in saffron (*Crocus sativa*), and is a yellowish-red substance, freely soluble in alcohol, but much less freely in ether and water. When mixed with potassium hydrate in weak solution, it forms a reddish liquid, in

which an almost violet flocculent precipitate appears on the addition of ether Nitric acid transforms its colour to green, and sulphuric acid, if strong, to blue.

It is chiefly obtained by the decomposition of *polychroite*, a glucoside which exists in saffron to a much more considerable extent than crocin.

By heating with dilute acids, *crocetin* and a form of sugar resembling glucose, but known as *crocin sugar*, are produced.

The equation, which involves the taking up of water, has not yet been worked out.

ELATERIN. Formula, $C_{20}H_{28}O_5$.

Is stated to be contained to the extent of 20 per cent. in *elaterium*, B P, the flocculent matter which falls when the juice of the "squirting cucumber," *Ecballii fructus*, is allowed to subside after expression.

Elaterin is soluble in alcohol, and may be separated from the starch and fibre, co-existent with it in elaterium, by treating with boiling spirit. If the spirituous solution be evaporated, and mixed with sodium hydrate dissolved in hot water, the resinous contamination of the elaterin will be converted into a saponaceous sodium salt, and the pure glucoside be deposited in crystals. Absolute freedom from foreign matters is secured by several recrystallizations from spirit.

The glucosidic nature of elaterin is doubtful; it is, however, certain that elaterium contains a glucoside, because it yields glucose when boiled with dilute sulphuric acid, but whether or not this glucoside be elaterin, which does not invariably give this reaction, is as yet an open question

The amount of elaterin *elaterium* will yield, is made by the Pharmacopœia to constitute an important test, as will be seen from the following:—

Characters and Tests In light friable slightly incurved cakes, about one line thick, greenish grey, acrid, and bitter, fracture finely granular. Does not effervesce with acids; yields half its weight to boiling rectified spirit. This solution, concentrated and added to warm solution of potash, yields on cooling not less than 20 per cent. of elaterin in colourless crystals.

DIGITALIN. Formula, $C_{27}H_{45}O_{15}$.

This is the official *digitalinum*, B P., and is directed to be prepared from the leaves of *Digitalis purpurea*, B P, by the undermentioned process -

Digest 40 ounces of digitalis with a gallon of the spirit, for twenty hours, at a temperature of 120°, then put them into a percolator, and when the tincture has ceased to drop, pour a gallon of spirit on the contents of the percolator, and allow it slowly to percolate through Distil off the greater part of the spirit from the tincture, and evaporate the remainder over a water bath until the whole of the alcohol has been dissipated. Mix the residual extract with five ounces of distilled water to which half an ounce of acetic acid has been previously added, and digest the solution thus formed with a quarter of an ounce of purified animal charcoal, then filter and dilute the filtrate with distilled water until it measures a pint. Add solution of ammonia nearly to neutralization, and afterwards add one hundred and sixty grains of tannic acid dissolved in three ounces of distilled water. Wash the precipitate that will be formed with a little distilled water; mix it with a small quantity of the spirit and a quarter of an ounce of the oxide of lead, and rub them together in a mortar Place the mixture in a flask, and add to it four ounces of the spirit; raise the temperature to 160 F, and keep it at this heat for about an hour, then add a quarter of an ounce of purified animal charcoal, put it on a filter,

and from the filtrate carefully drive off the spirit by the heat of a water bath. Lastly, wash the residue repeatedly with pure ether, and then dry it.

In this process the *digitalin* is dissolved out from the alcoholic extract by diluted acetic acid, and the solution partially decolorized and nearly neutralized. It is precipitated by tannic acid, which forms a tannate of digitalinum. On rubbing this with plumbic oxide and alcohol, plumbic tannate is formed, and the digitalinum set free, which dissolves in the alcohol.

The amorphous substance prepared as above contains an inactive impurity, insoluble in chloroform; thus it may be readily separated from the pure glucoside, which dissolves in that menstruum. By this method an uncrystallized product is obtained, which, however, assumes the definite form of acicular crystals agglomerated into star-like masses when crystallized from alcohol. When boiled with a dilute acid, glucose is formed, together with a body exclusively formed by the decomposition of digitalin, known as *digitaliretin*, thus :—

$$C_{27}H_{45}O_{15} + 2H_2O = \underset{\text{(Digitaliretin.)}}{C_{15}H_{25}O_5} + 2C_6H_{12}O_6.$$

Digitalin is usually met with in porous mammillated masses or small scales, white, inodorous, and intensely bitter; readily soluble in spirit, but almost insoluble in water and in pure ether; dissolves in acids, but does not form with them neutral compounds; its solution in hydrochloric acid is of a faint yellow colour, but rapidly becomes green. It leaves no residue when burned with free access of air. It powerfully irritates the nostrils, and is an active poison.

GUAIACIN. Formula, $C_{20}H_{23}O_5$.

The exudation from *Guaiacum officinale* consists of this glucoside, together with *guaiaretinic acid.* The result of boiling the resin with dilute acid, is the formation of *guaiaretin*, a resinoid body insoluble in water and of a greenish colour.

In contact with oxidizing bodies, such as chromic acid, oxygen, or even air, products of successive oxidation are formed, at first of a blue or green colour, but afterwards becoming brown.

If the resin be dissolved in alcohol, these reactions are exhibited to the best advantage. In consequence of the above-mentioned quality, a solution of guaiacum in alcohol forms one of the best tests for chromic acid. Gluten produces a similar effect to oxidants; starch, however, does not; but gum resembles gluten in its behaviour towards guaiacum, even if the impure form of guaiacum resin be used. The official resin is described as being in large masses of a brownish or greenish-brown colour; fractured surface resinous, translucent at the edges. A solution in rectified spirit strikes a clear blue colour when applied to the inner surface of a paring of raw potato.

GLYCYRRHIZIN. Formula, $C_{24}H_{36}O_9$ (?).

This is the sugar contained in the root of *Glycyrrhiza glabra*, and in an impure form constitutes *extractum glycyrrhizæ*, B.P.

When this glucoside is boiled with dilute hydrochloric acid, the decomposition which occurs is :—

$$C_{24}H_{36}O_9 + H_2O = \underset{\text{(Glycyrrhetin.)}}{C_{18}H_{26}O_4} + C_6H_{12}O_6.$$

It may be procured in a purer condition by making an aqueous extract of the root by maceration, and adding potassium hydrogen-tartrate to the clear

liquid. The precipitate which falls is treated with alcohol, the solution filtered and evaporated. The residue consists of pure glycyrrhizin.

When it has been thus purified it consists of an almost pure white amorphous substance, which, however, is very slightly yellow, and is darkened by sodium hydrate to an orange tint. It is thrown down from a solution by most mineral salts. The ordinary solvents take it up readily. If from its sweet taste it be regarded as a sugar, it must be classed amongst those which do not ferment.

SANTONIN. Formula, $C_{15}H_{18}O_3$.

This substance is one of the few official glucosides, being *santoninum*, B.P., which is thus directed to be prepared from the flower-buds of *Artemisia* :—

Boil 1 lb. of santonica with a gallon of water and 5 ounces of lime, in a copper or tinned iron vessel, for an hour, strain through a stout cloth, and express strongly. Mix the residue with half a gallon of water and 2 ounces of lime, boil for half an hour, strain, and express as before. Mix the strained liquors, let them settle, decant the fluid from the deposit, and evaporate to the bulk of two pints and a half. To the liquor, while hot, add, with diligent stirring, hydrochloric acid until the fluid has become slightly and permanently acid, and set it aside for five days that the precipitate may subside. Remove by skimming any oily matter which floats on the surface, and carefully decant the greater part of the fluid from the precipitate. Collect this on a paper filter, wash it first with cold distilled water till the washings pass colourless and nearly free from acid reaction, then with half an ounce of solution of ammonia previously diluted with five fluid ounces of water, and lastly with cold distilled water, till the washings pass colourless. Press the filter containing the precipitate between folds of filtering paper, and dry it with a gentle heat. Scrape the dry precipitate from the filter, and mix it with animal charcoal. Pour on nine ounces of rectified spirit, digest for half an hour, and boil for ten minutes.

Filter while hot, wash the charcoal with an ounce of boiling spirit, and set the filtrate aside for two days in a cool dark place to crystallize. Separate the mother-liquor from the crystals, and concentrate to obtain a further product. Collect the crystals, let them drain, redissolve them in four ounces of boiling spirit, and let the solution crystallize as before. Lastly, dry the crystals on filtering-paper in the dark, and preserve them in a bottle protected from light.

Thus prepared, santonin is met with in colourless flat rhombic prisms, feebly bitter, fusible and sublimable at a moderate heat; scarcely soluble in cold water, sparingly in boiling water, but abundantly in chloroform and in boiling rectified spirit. Sunlight renders it yellow; not dissolved by diluted mineral acids; entirely destructible by a red heat with free access of air. It dissolves in water in the presence of sodium carbonate, if sufficient be present to form an alkaline salt, which possibly occurs in consequence of santonin being an acid, though not of a well defined nature. The ammonium salt cannot be formed by the direct action of ammonium hydrate, but calcium santonate being soluble in water, while the ammonium compound is not, the latter may be directly formed by precipitation from the former. The characteristic reaction of all glucosides is in this case accompanied by the formation of a resinoid body (which is soluble in alcohol, but not in water, and is known as *santoniretin*) and glucose. When santonin is dissolved in a few drops of strong sulphuric acid and a dilute solution of ferric chloride added drop by drop (with constant agitation), a fine violet colour is produced.

CONVOLVULIN. Formula, $C_{31}H_{50}O_{16}$.

Is contained to a large extent in *jalapa*, B.P., and is converted on boiling with a dilute acid into glucose and convolvulinol, thus:—

$$C_{31}H_{50}O_{16} + 5H_2O = C_{13}H_{24}O_3 + 3C_6H_{12}O_6.$$

It is also the chief portion of *jalapæ resina*, B.P., and is left insoluble when that body is treated with ether. It is insoluble in turpentine, while common resin dissolves; and its presence may be therefore detected by the use of that menstruum.

JALAPIN. Formula, $C_{34}H_{56}O_{16}$.

Is the chief part of *scammoniæ resina*, B.P., and also exists in jalap resin to a small extent. Dilute acids boiled with jalapin will resolve it into glucose and *jalapinolic acid*, thus:—

$$C_{34}H_{56}O_{16} + 5H_2O = C_{16}H_{30}O_3 + 3C_6H_{12}O_6.$$

Jalapin is taken up by ether without reference to proportion. On account of the value of scammony resin, it is frequently sophisticated with the resins of jalap, pine, and guaiacum. One of the best tests for scammonin,—which however is only reliable in the absence of ordinary resin,—is sulphuric acid, by which a red coloration is caused. The official substance, *scammonium*, contains 80 to 90 per cent. of the resin, the remainder being gum. Guaiacum resin may be detected by the blue colour formed when it is treated with oxidizers, such as a mixture of potassium dichromate and sulphuric acid; and jalap resin (convolvulin) by the impure jalapin not being entirely soluble in ethyl oxide.

It is an unfortunate confusion of names which denominates the active portion of scammony resin *jalapin*, and of jalap resin *convolvulin*; but such is the present nomenclature, and we can only bow to it.

COLOCYNTHIN. Formula, $C_{56}H_{84}O_{23}$.

Is an extremely bitter and powerfully purgative body, constituting the active principle of colocynth (*colocynthidis pulpa*, B.P.,) from which it is prepared by infusing the pulp with water, and treating the clear liquid with plumbic acetate and animal charcoal. The latter absorbs the colocynthin (as it does also the bitter principle of gentian when that root is similarly treated). On boiling the charcoal with water, the colocynthin is again taken up, and to the solution charcoal is once more added. Separation of this latter charcoal and treatment with boiling alcohol is next necessary, and if the solution be immediately poured off and allowed to cool, a pure product separates out as the temperature decreases.

Colocynthin, when dissolved in either water or alcohol (it is insoluble in ether), is usually thrown down by metallic salts in a gelatinous condition.

The action of a dilute acid is attended by decomposition into colocynthein, which is a resin, and glucose:—

$$\underset{\text{(Colocynthin.)}}{C_{56}H_{84}O_{23}} + 2H_2O = \underset{\text{(Colocynthein.)}}{C_{44}H_{64}O_{13}} + 2C_6H_{12}O_6.$$

ÆSCULIN.

Æsculin is a constituent of the variety of chestnut known popularly as the "horse chestnut."

Several formulæ have been assigned to this principle; but the present state

of uncertainty warrants us in holding our opinion as to the correctness of any of them in abeyance. It is a white crystalline substance, which may be thrown down from an aqueous solution by plumbic acetate, which acts upon cupric solutions like glucose, is turned red by chlorine, and is much less soluble in alcohol and in water when they are cold than when they are hot. Its most characteristic property is the exhibition of a bluish fluorescence when such of the rays of light as are unable to render ordinary objects visible (technically called the "ultra violet rays") fall upon a solution.

An accompanying body, paviin, gives rise to a greenish fluorescence when these rays fall upon its solution.

ARNICIN.

Does not appear to have been well isolated, as the formulæ given differ much. It is stated to be a yellow bitter substance, incapable of crystallization, much more easily soluble in ether than in water, and yielding a brown precipitate together with glucose, when boiled with dilute acids. It possesses the odour and taste of arnica.

CHIRATIN.

This is a yellowish neutral glucoside, and to it are attributed the medicinal effects produced by *chirata*, B.P.

GELATIN.

Is a glucoside belonging to a class which might appropriately be named *glucosamides*, as it yields an ammonium salt when boiled with a dilute acid. It is contained in almost all parts of the body except the cartilages, and when extracted by boiling water becomes semi solid on the cooling of the solution. If however pure glycerin be substituted for the water, gelatinization does not occur as before, thus indicating that the gelatin requires to enter into a species of combination with the water in order to form a true jelly.

Isinglass, B.P., is the purest form of gelatin, and is stated to be:—

The swimming bladder or sound of various species of *Acipenser*, *Linn.*, prepared and cut into fine shreds.

Gelatin in solution yields a precipitate when treated with a solution of tannic acid. This is exactly the same in composition as ordinary leather, and is of a greyish tint. Its formation becomes a useful test both for tannic acid and gelatin. Aluminium salts, plumbic acetate, and plumbic oxyacetate give no result when added to dissolved gelatin. A 10-grain to the ounce solution in water is official as a test for tannic acid. Size and glue both consist of gelatin in a more or less impure condition.

CHONDRIN. Formula, $C_{24}H_{40}N_6O_{10}$.

Is a body performing those functions in the cartilages which gelatin performs in the muscles and bones. It gives precipitates with substances which do not affect gelatin; for instance, alum, organic acids, plumbic acetate, and plumbic oxyacetate.

It might be supposed from the name, that *Chondrus crispus*, B.P. (Irish moss), would contain chondrin; but instead of this being the case, the principal constituent is—

PECTIN. Formula, $C_{32}H_{48}O_{32}$.

This body is that which causes cooked fruit to assume a kind of gelatinous consistence on cooling. It is soluble in water, and is not rendered opaque

by drying. By prolonged contact with pectin or any of its isomers (of which several exist, all like itself devoid of taste) alkalies form **pectates**, the acid of which is said to have the formula, $C_{16}H_{22}O_{15}$, and to be insoluble in water.

SMILACIN, or PARILLIN.

Has not been much investigated, even its formula being uncertain.

It is composed of clear, colourless, and odourless crystals, of an acicular form and soluble in alcohol. When treated with strong sulphuric acid, a solution of a red colour results, which is not permanent, as it passes into a purplish and afterwards to a yellowish tint, which is due to the co-existence of unchanged red, and a green colour.

Water does not dissolve smilacin.

SAPONIN. Formula, $C_{12}H_{20}O_7$.

This is a constituent of the root of the pink and some other plants, which derives its name from existing in *Saponaria officinalis*, the *soap wort*. Like the root of this plant, when shaken or beaten up with water, it yields a lather. It has been said to be identical with smilacin; and another glucoside,—polygalic acid (the active principle of senega root),—is supposed to form it by decomposition.

THE ALOINS.

These bodies have been investigated to such an extent that the idea formerly held of their being glucosides has been disproved Unfortunately, however, experiments have not been made with sufficient certainty to enable their exact classification, although the strong presumption is that they are members of the *phenol* series. This idea is supported by the facts (1) that they may be made to yield sulpho salts similar to hydrogen phenyl-sulphate; (2) that with ferric chloride they produce a greenish coloration; and (3) that under the influence of nitric acid they yield such products as picric acid

The aloin obtained from a sample of aloes differs according to the botanical origin of the juice, and we have :—

BARBALOIN.

This body is obtained from *Barbadoes aloes* by boiling one pound with a gallon of water slightly acidulated with sulphuric acid. The solution thus obtained having been allowed to stand for twenty-four hours to deposit resinous matter, is poured off, quickly concentrated by evaporation to about thirty ounces, and set to crystallize. The crystals of aloin obtained are purified by re-crystallization from very dilute spirit Barbaloin is in yellow prismatic crystals, very soluble in water, alcohol, and ether. Its solution gives with bromine water a yellow precipitate of brom-aloin, and the solid itself turns red when treated with nitric acid, the colour rapidly fading When subjected to a lengthened treatment with nitric acid, it yields both picric and chrysamic acids. It begins to melt at 300° F.

SOCALOIN, or ZANALOIN.

The aloins of *Socotrine*, *Zanzibar*, and *Cape aloes* very closely resemble barbaloin: but, according to Rochleder, **socaloin** must be regarded as distinct. It is much less soluble in ether than barbaloin, and commences to melt at 245° F.

NATALOIN.

May be isolated from *Natal aloes* by a similar process to the aloins already described. It crystallizes in plates, and is only slightly soluble in water and alcohol. The red colour produced by strong nitric acid with nataloin does not fade, as in the case of barbaloin, and it gives no precipitate with bromine. Treated with nitric acid it yields picric and oxalic acids, not chrysamic acid.

According to the authority already quoted, the figures obtained in the analysis of the aloins correspond equally well to formulæ only half as great, and when viewed by this light we have a new homologous series, as follows :—

Socaloin	$C_{15}H_{16}O_7$.
Nataloin	$C_{16}H_{18}O_7$.
Barbaloin	$C_{17}H_{20}O_7$.

Differing from each other by the constant increment CH_2. Since this, Tilden has shown that really anhydrous barbaloin and socaloin are isomeric, and have the formula $C_{16}H_{18}O_7$; and if this be so, then the three are all the same thing, only varying in hydration. It is to be hoped that further researches will put the whole matter of the aloins on a firmer basis.

CHAPTER XXI.

ALBUMINOUS AND PIGMENTARY BODIES.

I. ALBUMINOUS BODIES.

ARE a class by themselves, and form the principal portion of the solid matters of which the animal frame is built up; they also exist, though not to so large an extent, in the tissues of vegetables.

ALBUMEN. Formula uncertain.

The white of egg (*albumen ovi*, B.P.) is a very pure form of this body in union with a small proportion of a membranous substance insoluble in water and removable by subsidence after shaking up the white of egg with that solvent. A solution containing 2·5 to 3·5 per cent. (the white of one egg to four ounces of water) is the *solution of albumen* employed by the B.P. as a test. When heated to temperatures above 180° F., albumen forms *coagula*, such as most persons have observed floating in the water in which an accidentally cracked egg has been boiled. In consequence of many salts, especially those of mercury, silver, lead, aluminium, and tin, forming insoluble compounds with albumen, it is a useful antidote for metallic poisons. The insoluble compound must, however, be immediately removed by a stomach-pump, otherwise absorption into the system will occur, in spite of the insolubility of the albumen compound. Carbo-acids generally, such as acetic and tartaric, do not coagulate albumen; but tannic acid is an exception to this rule. Mineral acids, such as nitric, hydrochloric, and sulphuric, when added to a solution of albumen, give a precipitate in the cold, which, on heating with excess, dissolves, with the formation of a colour varying from yellow (when nitric acid is taken) or blue (when hydrochloric is employed) to reddish or purplish-brown. Alkalies dissolve the precipitate which mineral acids form, and if pure solid albumen (obtained by the addition of alcohol to an aqueous solution) be introduced in a weak alkaline solution, it dissolves readily.

The approximate composition of white of egg is :—

Salts	0·3	or	Fibrinous Matter, etc.	4·2
Mucus	2·7			
Albumen	12·0		Albumen	15·0
Water	85·0		Water	80·8
	100·0			100·0

A variety of albumen existing in the serum of blood (the colourless liquid in which the corpuscles are suspended) differs from that of the egg by not yielding a coagulum with ether, as the latter does. White of egg, under the French

technical name of *glaire*, is used to impart a gloss to cards, the covers of books, and other surfaces. It is also employed as a clarifying agent, acting by forming an insoluble compound with some constituent of the liquid into which it is introduced, which compound can be removed either by allowing it to settle and then drawing off the clear liquid, or by skimming. Occasionally it is requisite to apply heat in order to throw down the albumen, and in this case the coagulum encloses mechanical impurities, consequently, when the whole is removed, a clear liquid is left.

It is as yet unknown whether any chemical change occurs on heating albumen until it coagulates. The contents of the lacteal and lympathic vessels have albumen as one of their constituents ; and in the brain, the muscles, and the organs connected with digestion and excretion, this substance is also to be found. Inflammation of the glands concerned in the secretion of saliva, bile, gastric juice, and mucus, cause these substances to contain albumen, though normally it is absent from them. Its presence in the urine is an indication of serious functional derangement of the kidneys. The great difficulties in the determination of the formula of such a complex compound as albumen, render those experiments which have from time to time been made, with the view of obtaining it, by no means absolutely reliable. It is probable, however, that $HNaC_{72}H_{110}N_{18}SO_{22}.H_2O$ is approximate to the truth. This composition resembles that of gelatin, which contains rather more nitrogen, and rather less carbon and hydrogen.

The yellow yolk, or yelk, of egg is used in the B.P. for making *mistura spiritus vini Gallici*, under the name of *ovi vitellus*. It contains phosphorus as well as sulphur, and besides this differs chiefly from the white in containing some casein, and yellow oily and fatty matters to the extent of about 29 per cent. These fatty matters may be dissolved out of the coagulated yolk by treatment with warm alcohol and ether. Seventeen per cent. of albuminous bodies are said to be contained in yolk of egg ; but whether this be wholly or only in part albumen is uncertain. In the presence of gum, or such salts as potassium nitrate, calcium chloride, or magnesium sulphate, acetic acid gives a precipitate with albumen, though otherwise it does not. On the addition of plumbic acetate to the serum of blood, a compound is obtained which, when suspended in water, through which a stream of carbonic anhydride is passed, yields on filtration an opalescent solution of albumen. This, when heated to 160° to 164° F., coagulates completely, the reaction commencing at 140° F.

By exposing a thin layer of white of egg, spread upon a glass or metal plate, to dry air, a yellowish film is procured, which does not decompose by keeping for any length of time, unless it become damp. When an egg is boiled, a trace of an alkaline sulphide is formed, hence the blackening of silver articles when left in contact with it. A distinct black precipitate, of more or less impure plumbic sulphide, results from heating albumen with potassium hydrate and plumbic acetate.

CASEIN.

Is the nitrogenous constituent of milk, giving to that liquid its great nutritive value.

It differs from albumen in not being found in the tissues, muscles, or in the blood.

Milk yields it in the purest condition by treatment with magnesium sulphate in crystals ; a precipitate falls, which should be collected upon a filter and washed with a strong solution of magnesium sulphate dissolved in pure water

The floating fatty matter is skimmed off, and then, acetic acid being used to form a coagulum, almost pure casein is obtained.

Milk contains 3 to 3·5 per cent. of casein, which itself contains a metal, and ought probably to be regarded as a salt. Casein dissolves in water more readily if it be slightly alkaline than otherwise, and may be distinguished from albumen by not coagulating when a solution of it is boiled, and by being coagulated by acetic acid. When this acid is added to milk, the casein is rendered insoluble, but it also takes with it the fatty matters. The metallic salts which throw down albumen, also precipitate casein. By exposure to dry air casein becomes dehydrated, and then refuses to redissolve in water.

When treated with potassium hydrate, most albuminoids form *albuminate*, or *protein*, which bears a great resemblance, in some cases, to casein.

If strong hydrochloric acid be substituted for potassium hydrate, *syntonin*, or *para-peptone*, is produced.

FIBRIN.

Results from the action on each other of two albuminoids contained in blood-serum, and in the serum of the pericardium, of the lymphatics, and of the lacteals. Both dissolve in saline solutions, if an excess of sodium chloride be not present, as well as in dilute acid and alkalies. The formation of fibrin takes place most readily at about 100° F., and it is also produced much more freely in contact with dead, or unorganized, than with organized matters. Fibrin, as formed by the interaction just mentioned, is a gelatinous and transparent, or a flocculent solid. It may also be prepared from blood, by agitating it with a bundle of twigs or wires, removing the blood corpuscles (by washing with water) from the adherent pseudo-coagulum, and, after drying slightly, treating with ether, to dissolve out fatty contaminations. At 162° F. fibrin is converted from a transparent into a translucent condition. When it is treated with water acidulated with hydrochloric acid, and the mixture evaporated to dryness in a water-bath, an "amyloid substance" is produced, resembling coagulated albumen, but which is acted upon by iodine with the production of a red colour, and gives, with the same reagent, after previous treatment with sulphuric acid, a purplish reaction. When flesh undergoes digestion in the stomach, the first product is para-peptone; but this is quickly converted into an albuminous body called *peptone*, which, unlike most varieties of albumen, is neither thrown out of a solution by alkalies nor acids. Fibrin was formerly believed to be the principal nutritive or nitrogenous constituent of flesh; but the name *myosin* is now applied to a body which appears to occupy this position. Myosin differs from fibrin in its greater and more complete solubility in sodium chloride solution.

HÆMO- or HÆMATO- GLOBIN.

Is the colouring principle existing in blood, and contains 0·4 per cent. of iron. If two parts of the liquid left upon separating the fibrin from blood be mixed with two parts of water, and one part of alcohol then added, after the lapse of a day crystals are produced. These, after pressure and re-solution in water, may be treated with alcohol as before; and after this process has been repeated several times, pure crystals of hæmoglobin result. They are of a red colour, and freely absorb oxygen from the air, especially when moist. The red colour of the natural crystals becomes purplish in the presence of carbonic anhydride; and the existence of blood in a venous or arterial condition depends upon the relative quantities of oxygen and carbonic anhydride it contains The oxygen absorbed by hæmoglobin cannot be indicated by the

addition of nitric oxide gas (NO), hence a true compound must be formed. This combination, however, is not stable, because all acids (even a solution in water of carbonic anhydride) decompose it, and no means is known by which it can be thrown down from an aqueous solution unaltered. Carbonic oxide forms a compound of a reddish colour with hæmoglobin, after driving out the oxygen dissolved in it; hence the very prejudicial effect following the accidental inhalation of that gas. The natural condition of hæmoglobin in the blood being more or less oxygenated, it is acted upon by hydrogen sulphide, sulphur separating, and an albuminoid body being at the same time produced by the splitting up of the colouring principle.

A dark blue crystalline substance (named *hæmatin*, and containing about 9 per cent. of iron), in union with a form of albumen, termed *globulin*, is believed to compose hæmoglobin.

PTYALIN and PANCREATIN.

These exist in saliva and the pancreatic juice respectively, and both serve the office of converting amylaceous or farinaceous into saccharine bodies, the latter serving also to assimilate fatty substances. They may be obtained pure by processes which are rather troublesome; but if first a solution of phosphoric acid, and then one of calcium hydrate be added to a solution of either, precipitates may be obtained, which, though not of absolute purity, are equally efficacious as remedial agents. Ptyalin and pancreatin appear to act best in the presence of a trace of alkali, and to have their power of forming sugar from starch destroyed completely by heating to 212° F. They may, however, be dried at 60° to 80° F. without alteration.

PEPSIN.

Has been employed in France and England as an aid to digestion for some time past, and exists naturally in the gastric juice. In the presence of a dilute acid (in the human stomach said to be hydrochloric, in that of the dog, lactic, acid), pepsin dissolves coagulated albumen, and bodies resembling it, with the formation of *peptone*. It is prepared from the washed mucous lining of the stomach of the calf, sheep, or pig, by scraping with a knife, and macerating the slimy product, thus removed, with cold water, by which means a solution of pepsin results. When this solution is mixed with dilute phosphoric acid, and then calcium hydrate solution is added, the pepsin is carried down with the precipitate of tricalcium phosphate. This precipitate may itself be used medicinally, and in fact, when the stomach of the pig is used, sometimes constitutes the mixture commercially known as *pepsina porci*. A tincture may be formed by digesting it with spirit and a little acid; and a wine has likewise been prepared which is in extensive use. The powder should not be dried at a temperature exceeding 100° F. by more than 5° to 15° F.

A common form of pepsin is simply a mixture of the moist scrapings of the stomach with rice starch dried at a gentle heat.

When plumbic acetate is added to a clear solution of pepsin, a precipitate containing the pepsin falls; and this, when decomposed with sulphuretted hydrogen in excess, and the slightly warmed mixture filtered, yields a solution of pure pepsin. Upon evaporating this liquid at 100° to 115° F. the solid remains. The pepsin obtained from the pig is best adapted for aiding human digestion, man being, like each member of the porcine family, an omnivorous animal, and it being highly probable that the pepsin of herbivorous animals is only specially suited for the digestion of vegetables.

Commercial pepsin is a light powder, of a greyish-white colour. It has

an unpleasant taste and odour, and when yielded by herbivorous animals this odour is somewhat acid. It is rendered inactive by being heated to 120° F.

It is only when impure that mercuric salts and tannic acid give a precipitate with a solution of pepsin. The B.P. thus directs and describes :—

A preparation of the mucous lining of a fresh and healthy stomach of the pig, sheep, or calf.

The stomach of one of these animals, recently killed, having been cut open and laid on a board with the inner surface upwards, any adhering portions of food, dirt, or other impurity are to be removed, and the exposed surface slightly washed with cold water; the cleansed mucous membrane is then to be scraped with a blunt knife or other suitable instrument, and the viscid pulp thus obtained is to be immediately spread over the surface of glass or glazed earthenware, and quickly dried at a temperature not exceeding 100° F. The dried residue is to be reduced to powder, and preserved in a stoppered bottle.

Characters and Tests.—A light yellowish-brown powder, having a faint but not disagreeable odour, and a slightly saline taste, without any indication of putrescence. Very little soluble in water or spirit. Two grains of it, with an ounce of distilled water, to which five minims of hydrochloric acid have been added, form a mixture in which 100 grains of hard-boiled white of egg, in thin shavings, will dissolve on their being digested together for about four hours at a temperature of 98° F.

GLUTEN.

This is the name applied to the elastic solid which is left when flour or any similar powdered farinaceous grain is washed on a sieve with water. (*See* **Starch.**) The pure substance which it yields on treatment with alcohol is termed *glutin*, and exists in gluten combined with vegetable casein and vegetable fibrin. The latter is slightly soluble in water; and if the crude substance be rubbed with water, and the clear liquid boiled, it coagulates exactly like albumen or fibrin. Wheaten flour yields a solution of vegetable casein, when it is agitated with alcohol. The casein separates upon evaporation as an adhesive mass, which, when dried completely, is horn-like in appearance. A considerable amount of vegetable albumen may be extracted from potatoes by bruising them with water containing a little sulphuric acid; and the liquid, when heated, behaves exactly like animal albumen.

LEGUMIN.

Is the vegetable casein to which we have just referred. It is contained in leguminous seeds, such as peas, almonds, or beans, sometimes to the extent of 10 to 12 per cent., and may be extracted by water. If the solution, which also contains sugar and gummy matters, be mixed with a drop or two of acetic acid, the legumin is coagulated, and falls. It may, however, be redissolved by potassium hydrate. A solution of legumin resembles casein in not being coagulated by boiling. It is true that if a solution of either be heated, a skin forms on the surface; but this is due to an oxidation of the legumin or casein, and not to any coagulation, as the liquid below remains clear. Alcohol in small quantity throws down both bodies. If a mixture of legumin and a saccharine solution be allowed to putrefy, lactic acid is formed.

All the albuminous bodies just considered are held to constitute the *flesh-forming* portion of food, in contradistinction to the amylaceous and saccharine, bodies which are simply *heat-producers.* Church has recently shown that the true flesh-forming albuminoids are distinguishable from the other nitrogenous compounds by being capable of coagulation by carbolic acid.

II. PIGMENTARY SUBSTANCES.

The majority of compounds possess colour, that is, exercise a selective influence upon white light, absorbing some particular rays and reflecting others. Let us, for instance, take the three principal tints exhibited by leaves at various seasons of the year. In spring they contain a colouring matter known as *chlorophyll*, which absorbs blue and red light, and reflects green, the white light containing these three. At the end of summer the leaves become yellow. This colour is due to the absorption of some red, and of blue, and the reflection of the mixture of green and red, which produces the impression of yellow. Towards the end of autumn the capability of reflecting green ceases, both it and the blue are absorbed, and the red, which are the only rays reflected, cause the leaves to appear of that colour. There is a popular idea that the colour of bodies is as much a quality as weight. This, however, is quite erroneous, because when a body is viewed in a light which it is incapable of either reflecting or decomposing, it appears black; thus a red body in green light appears black.

Substances which transmit all light rays equally well, are colourless: examples, most liquids and crystals, such as water and alcohol, also alum and Iceland spar.

Compounds which scatter light without absorbing one class of rays more than another, are opaque and white: examples, chalk or whiting (calcium carbonate), heavy white (barium sulphate), white lead (plumbic oxycarbonate); pearl white (bismuthic oxynitrate or oxychloride), zinc white (zinc oxide); gypsum (calcium sulphate); soapstone, French chalk, or steatite (magnesium silicate), stannic oxide, and calcium phosphate (both of which are useful in the manufacture of opal glass).

There are two classes of substances which absorb all rays equally and totally, or almost so, the few rays reflected being chiefly red.

1. **Brown.** Some few rays of red light are reflected: examples, many extracts, if evaporated at too high a temperature, become brown; such as *terra japonica* and catechu. Caramel is of the same nature. Sepia (the evaporated fluid of the "ink-bag" of several species of *sepiadæ*, or cuttle-fishes) Umber (which is darkened in colour by heating, and then forms *burnt umber*) and sienna, are ferric and aluminic silicates.

2. **Black.** Bodies which do not reflect sufficient light to affect the eye materially, and which would be invisible were all substances like them. Black dyes usually contain varieties of tannin combined with iron in the ferric state; sometimes, however, they contain aniline. Ink is a ferric gallo-tannate suspended in water by means of gum and sugar. Carbon is the basis of most black substances, for instance, lamp-, ivory-, and bone-black, and blacklead. The first of these, *i.e.*, lamp-black, when rubbed with boiled linseed oil, forms *printing ink*, and when mixed with hot glue or size, makes *Indian ink*.

Blue. Bodies which reflect blue rays only, and therefore bear that name. These are very abundant, especially in the vegetable kingdom. *Ultramarine* is purely mineral, and its exact composition is doubtful. It is the result of heating a mixture of sodium sulphate and carbonate with carbon, sulphur, and kaolin, in closed iron vessels, but was simply powdered *lapis lazuli* originally. Cobaltous oxide produces cobaltic ultramarine, Thénard's blue, cobalt, and Hoffner's blue, when combined with aluminium oxide and calcium phosphate in various proportions; whilst smalts, zaffre, Saxony, and king's blue, are characterized by the presence of sodium and silicic anhydride, thus being a kind of glass.

Copper, in the forms of "ortho-," oxy-, or hydrato- carbonates, constitutes blue malachite, English-, copper-, and mountain-blues. Paris-, Saxon-, Berlin-, or Erlanger- blue are various commercial names for mixtures of Prussian-blue and Turnbull's blue with white and other powders. Cudbear, archil, orchil, lichen-blue, and turnsole, are all a form of litmus, prepared, however, by different processes.

Litmus is prepared from the lichens known as *Variolaria tinctoria*, *Roccella orcina*, *Lecanora tartarea*, and others, by reducing them to a paste with water and ammonium carbonate (or an ammoniacal liquid such as putrid urine), and then exposing the mixture to the air, by which means a colouring matter is developed. The blue or purple matter may be dissolved out by slightly alkaline water, which yields it in a pure solid condition by evaporation. The formation of the blue is due to the action of oxygen in the presence of ammonium hydrate or carbonate, on orcin, $C_7H_8O_2$, by which orcein, $C_7H_7NO_3$, is generated, the following being probably the reaction:—

$$2C_7H_8O_2 + 2NH_3 + 3O_2 = 2C_7H_7NO_3 + 4H_2O.$$

Even orcin itself, however, is not contained as such in lichens, its production arising from the decomposition of orsellenic acid, by alkalies, thus:—

$$\underset{\text{(Orsellenic Acid.)}}{C_8H_8O_4} + 2NH_3 + H_2O = (NH_4)_2CO_3 + \underset{\text{(Orcin.)}}{C_7H_8O_2}.$$

Litmus is used for preparing the B.P. test-papers, *red litmus paper* and *blue litmus paper*, and also the official *tincture of litmus*. The latter is thus directed to be made:—

Take of

Litmus, in powder	1 ounce.
Proof spirit	10 fluid ounces.

Macerate for two days in a closed vessel, and filter.

The papers are made by dipping unsized white paper (blotting or filter paper) into the tincture of litmus, and drying by exposure to the air. To prepare the red paper, the litmus must be "reddened by the addition of a very minute quantity of sulphuric acid." Faraday recommended simple exposure to the vapour of any fuming acid.

Indigo is a product obtained by the fermentation of many plants of the genus *Indigofera*, which sets in when they are macerated with warm water in open vessels, exposing a large amount of surface to the air. Oxidation is also promoted by agitation with oar-like implements wielded by men called "beaters" who stand in the solution. The plants themselves contain no indigo, this being formed by the spontaneous decomposition of a yellow substance termed *indican*, which is soluble in water, into the insoluble indigo, and a soluble sugar-like body, "indiglucin." Commercial indigo only contains about 50 per cent. of indigotin or true indigo, the rest being indigo red, and green colouring matter from the plant. Indigotin is insoluble in almost every compound, except strong fuming sulphuric acid. It is of less specific gravity than water when pure, gives a copper-red streak when rubbed, and possesses the formula C_8H_5NO. Dissolved in paraffin or aniline by heat, and the solution allowed to cool, after having been poured off from the insoluble portion, if any, acicular crystals separate out. Crystals of a coppery appearance may also be produced by mixing two parts of calcium sulphate with one part of indigo, and making the powder into a paste with water. When this paste is spread upon an iron plate, allowed to harden, and afterwards cautiously heated, the indigo is volatilized as a purple vapour. At a temperature only slightly above that of volatilization, the product becomes charred. It dis-

solves in alkalies in the presence of reducing agents, such as ferrous sulphate, to form a colourless solution. In this way the "indigo-vat" of the dyer is made. Two pounds of ferrous sulphate (in its commercial form of green vitriol) are dissolved in five quarts of water, and a mixture of three pounds of calcium hydrate (slaked lime) and one pound of powdered indigo, are added, and the whole well agitated in a closed (or covered) vessel. When the action, which consists in the production of ferrous hydrate, and the reduction and solution of the indigo by that substance in the presence of calcium hydrate, has ceased, the solution will deposit the white "reduced indigo" in the fibres of cloth, and the action of the air will reconvert this into indigo blue.

The B.P. solution of sulphate of indigo is really a solution of sulphindigotic or sulphindylic anhydride, $C_8H_4NO.SO_3$, and is directed to be prepared as follows :—

Take of

Indigo, dry and in fine powder	5 grains.
Sulphuric acid	10 fluid ounces.

Mix the indigo with a fluid drachm of the sulphuric acid in a small test-tube, and apply the heat of a water-bath for an hour. Pour the blue liquid into the remainder of the acid, agitate the mixture, and, when the undissolved indigo has subsided, decant the clear liquid into a stoppered bottle.

Free chlorine and nitric acid destroy its colour; the former producing, when distilled subsequently (after partial neutralization of the sulphuric acid), a substance (tri-chlor-aniline) from which aniline, C_6H_7N, may be procured by the action of sodium amalgam and water (*i.e.*, of nascent hydrogen). Nitric acid yields picric or carbazotic acid, $C_6H_3(NO_2)_3O$.

Green.—It was formerly believed that this was a compound colour, due to the absorption of red rays, and the reflection of blue and yellow. This idea, however, is no longer tenable; the celebrated physicist, Professor Helmholtz, having shown that, although two powders, one of which is yellow and the other blue, produce green when mixed, yet if one be so placed that the impression of the separate powders fall upon the same part of the eye, the combined light is white. In the case of mixing powders, however, the complicated nature of the rays which such a body as a blue powder reflects, prevents the application of this theory; and the practical rule, that a yellow and a blue substance when mixed give green, will remain unaltered in spite of the more extended knowledge of the nature of colour we now possess, due to Professors Helmholtz and Clerk Maxwell.

Leaves contain a green substance passing by the name of *chlorophyll*, which dissolves in alcohol and ether, though not in water, because it is of a resinous nature. It is contained in the expressed juice of plants, becomes flocculent on heating this liquid, and is then separated by a calico filter in preparing five of the official extracts, namely, those commonly called *green extracts*. When heated to much above 130° F., it becomes brown in colour. It is believed that chlorophyll (leaf green) is composed of *phyllo-xanthin*—leaf-yellow, and *phyllo-cyanin*—leaf blue. The colour of autumn leaves (due to chromule) is said to arise from the fading of the phyllo cyanin, the yellow remaining permanent for a longer time. Cupric and chromic oxides are used as green colourings for ceramic wares. A mixture of almost any yellow with a blue pigment, will give green. Many green colours contain copper, sometimes combined with arsenic. Such are Schweinfurth, Brunswick, verditer, and malachite greens. Buckthorn juice (*rhamni succus*, from *Rhamnus catharticus*, B.P.) when evaporated with calcium hydrate, gives *vegetable*, or

sap-green, a colouring principle which oils and ether do not dissolve, and alcohol only to a small extent, but which is readily soluble in water.

Yellow.—Was formerly fancied to be one of the three primary colours, but is now known to be due to the presence of red in green, because it is found that when blue light is mixed with green, and then a proportion of red is added, a yellow light is the result. The number of bodies which give the impression of yellow is very large, and it will therefore be convenient to name them in classes.

The three divisions we shall make are :—

I. Those of a mineral nature.
II. Carbonaceous substances of well-known composition.
III. Carbonaceous substances of greater complexity, such as resins.

I. Orpiment (arsenious sulphide, As_2S_3). Ochre is of many varieties, and passes, amongst others, by the following names: Chinese yellow, gold-ochre, gold-earth, and yellow sienna. It is a mixture of calcium, aluminium, and ferric oxides and hydrates. Chrome yellow is of the deepest colour when it contains least chromium, and reflects the most light when it contains the least amount of lead.

II. Carbazotic or picric acid, $C_6H_3(NO_2)_3O$, is that which yields the yellow dye most frequently used for silk. Combined with metals, it forms explosive compounds. The bark of *Quercus tinctoria*, or quercitrin, $C_{18}H_{20}O_{11}$.

Rhubarb owes its yellow colour to rheic acid, rhein, rhaponticin, rhubarbarin, rumicin, or rheumin, all of which are the names applied by various writers to chrysophanic acid, $C_{10}H_8O_3$. The colour is likewise probably due, though to a less extent, to *emodin*. The former body is the source also of the colour of *Parmelia Parietina*. Chrysamic and chrysolepic acid are also yellow colouring matters, and are formed artificially from aloes by the action of nitric acid.

Persian berries contain a substance of a yellow tint, termed chrysorhamnin, $C_{23}H_{22}O_{11}$, and are themselves the fruit of the *Rhamnus infectorius*. *Purree*, or *Indian yellow*, the exact source of which is unknown, consists essentially of magnesium euxanthate or purreate, $Mg2C_{21}H_{17}O_{11}$. Gambogic acid, $C_{20}H_{23}O_4$, constitutes the principal part, 70 to 80 per cent., of gamboge (*cambogia*, B.P.).

III. Fustic, or the yellow wood of *Rhus cotinus*, contains a yellow principle soluble in water. Carrots, when dried, and digested with carbonic disulphide, give a solution of carrotin, which, when procured in the solid form by evaporation, is used, it is believed, for colouring butter.

Turmeric rhizome, improperly termed "root" (*Curcuma longa*), contains a yellow resin, curcumin, $C_{10}H_{10}C_3$ (?).

Weld (*Reseda luteola*) owes its tinctorial power to a principle termed "luteolin," $C_{20}H_{14}O_3$ (?). Saffron (the dried style and stigma of *Crocus sativa*, B.P.) is believed to consist essentially of a yellow colouring matter, "Polychroite, or saffronin," of unknown constitution. *Rhamnus frangula*, the black alder, contains a yellow principle, frangulin, $C_6H_3(HO)_3$.

Red.—These substances reflect principally the red rays; but if they reflect a very little green also, they possess an orange tint.

We shall classify them similarly to the yellow.

I. Mercuric sulphide, HgS, is variously known as vermilion, Paris red, cinnabar, and Chinese red. Ferric oxide, or oxyhydrate in the native state, passes by the names of red ochre, Armenian bole, colcothar, red earth, Indian red, mineral purple, burnt ochre, terra di Sienna, stone red, Berlin red, and English red. It is termed also mineral rouge, purple rouge, and polishing or jeweller's rouge. Glass is coloured red by the stanno-auric salt (purple of

Cassius), or, more commonly, by cuprous silicate, formed by the introduction of cuprous oxide. Plumboso-plumbic oxide, Pb_3O_4, is *red lead*. Plumbic oxychromate, $Pb_2O.CrO_4$, is chrome red; also, if containing rather more chromium, orange chrome.

II. Anchusin, $C_{35}H_{40}O_8$, is the resinous body, soluble in fats and oils, contained in alkanet root (*Alkanna*, or *Anchusa tinctoria*).

Carminic acid, $C_{14}H_{14}O_8$, is the source of the colour of cochineal (*coccus*, B.P.). It is soluble in water, but is thrown down by albumen, or by a mixture of an aluminium or stannic salt and an alkaline hydrate or carbonate. The two precipitates, commercially denominated *carmine* and *carmine-lake* are treated with ammonium hydrate; if pure, they dissolve easily and completely. The first is absolutely soluble in ammonium hydrate, and this is an infallible test for the genuineness of the article. One method of procuring carminic acid in the pure state, is to precipitate a solution with plumbic acetate, and treat the lead compound—plumbic carminate—with hydrogen sulphide. To produce the true acid, free from all impurities, advantage must be taken of the fact that plumbic carminate will become converted into plumbic phosphate in the presence of phosphates (which normally exist with carminic acid in the *Coccus cacti*). Then other bodies may be removed from the still impure solid produced upon evaporation, by treatment first with alcohol, and then with ether, both of which dissolve carminic acid. A much simpler but secret process is known to be adopted in the manufacture of carmine.

The pure acid is of a purplish-red colour, and yields solutions in the three solvents, water, alcohol, and ether, of a most magnificent tint.

It is estimated, either in cochineal itself or in commercial carmine, by means of a solution of potassium permanganate (a check being made on pure carminic acid), and the amount of carminic acid present is indicated by the number of c.c. of the permanganate required to be added before a permanent pink coloration is produced. Various trade names are applied to a mixture of carmine with French chalk or starch.

Santalin, $C_{16}H_{16}O_3$, is the resinous colouring matter of *red sandal-wood* (*Pterocarpus santalinus*). Red-rose petals and red-poppy petals (*Rosæ Gallicæ petala* and *Rhœados petala*, B.P.), contain uninvestigated colouring principles.

Carthamin, $C_{14}H_{16}O_7$, exists to the extent of about a half per cent. in dyer's saffron, or safflower (*Carthamus tinctorius*). It forms a red powder when moist, and a green when dry, and a solution in alcohol possesses a purple colour. It was the colour formerly employed in making "pink-saucers," and is, when mixed with French chalk, the cosmetic termed *rouge végétal*. Carthamin is obtained pure by digesting "cotton-wool" in a solution obtained from the safflower by extraction with aqueous sodium carbonate, and adding acetic acid. The coloured cotton is then removed into a sodium carbonate solution, and when it is colourless, citric acid is employed to throw down pure carthamin from its alkaline solution.

Hæmatoxylin, $C_{16}H_{14}O_{16}$, is the red colouring substance developed in logwood (*hæmatoxyli lignum*, B.P.) by exposure to the air, and may be obtained in crystals. Its solution is darkened by alkalies, and rendered more bright in colour by acids.

Alizarin, $C_{14}H_8O_4$, is the red dye produced from madder (*Rubia tinctoria*), together with a similar body termed *purpurin*, $C_9H_6O_3.H_2O$, by the action of aluminium salts and a mineral acid. The former is best procured when aluminium chloride and hydrochloric acid are used, the latter when the sulphate and sulphuric acid are substituted.

Purpurin is obtained most abundantly when fermented solutions of madder undergo treatment. This is probably due to the decomposition of *rubian*, a yellowish principle existing naturally in madder. The action of sulphuric acid

on madder produces *garancin*. A solution of alizarin in sulphuric acid is of a splendid red tint, but an alkaline solution is purple. Water and alcohol do not dissolve it freely.

Alizarin is frequently prepared artificially from *anthracene*, $C_{14}H_{10}$, a white solid contained in tar. This process has been already detailed (*see page* 217).

III. *Brezilin*, which, united with aluminium hydrate, or a similar body, constitutes several "lake dyes," is produced from Brazil-wood, and is also probably contained in Cam- and Sapan- wood.

Annatto (also known as arnotto) owes its orange-red colour to a mixture of a yellow substance (orellin) and a red (bixin), both being named from the plant (*Bixa orellana*) in which they are contained. Annatto is commercially seen in cakes, which are manufactured from the seeds of the plant.

Lac-dye is an inferior and less expensive form of carmine, which is produced by insects of a similar nature to the *coccus*, having, however, their habitat in Southern Europe instead of the New World. The dye is not extracted from their bodies, but from a resinous substance of which they cause the deposition in the plants on which they live.

APPENDIX A.

Showing the Quantities of the various Ingredients (in parts by weight) to be added to 100 parts of Alcohol to produce the chief Artificial Fruit Essences.

Name of Ingredient.	Peach.	Apricot.	Plum.	Cherry.	Black Currant.	Lemon.	Pear.	Apple.	Grape.	Goose-berry.	Rasp-berry.	Straw-berry.	Melon.	Pine-apple.
Glycerin ($C_3H_5.3HO$)	5	4	8	3	...	5	10	4	10	...	4	2	3	3
Chloroform ($CHCl_3$)	...	1	...	...	...	1	...	1	2	...	...	...	...	1
Nitric ether ($C_2H_5NO_3$)	...	...	...	...	...	1	...	1	...	...	1	1	...	...
Aldehyd (C_2H_4O)	2	...	5	...	...	2	...	2	2	1	1	...	2	1
Acetic ether ($C_2H_5.C_2H_3O_2$)	5	...	5	5	10	10	5	1	...	5	5	5	...	...
Œnanthylic ether ($C_2H_5.C_7H_{13}O_2$)	5	1	4	1	2	...	...	...	10	1	1	...	...	...
Formic ether ($C_2H_5.CHO_2$)	5	...	1	...	...	...	...	...	2	...	1	1	1	...
Butyric ether ($C_2H_5.C_4H_7O_2$)	5	10	2	...	...	...	...	...	...	...	1	5	4	5
Valerianic ether ($C_2H_5.C_5H_9O_2$)	5	5	...	...	...	...	...	...	...	...	...	...	5	...
Benzoic ether ($C_2H_5.C_7H_5O_2$)	...	...	...	5	5	...	...	...	...	1	1	...	...	...
Sebacic acid ($C_{10}H_{18}O_4$)	1	...	...	...	...	...	...	...	...	...	1	...	10	...
Methyl salicylate ($CH_3.HC_7H_4O_3$)	2	2	...	...	...	...	...	...	1	...	1	1	...	...
Amyl acetate ($C_5H_{11}.C_2H_3O_2$)	...	...	...	...	...	...	10	...	...	...	1	3	...	...
Amyl butyrate ($C_5H_{11}.C_4H_7O_2$)	...	1	...	...	...	...	...	...	...	...	1	2	...	10
Amyl valerianate ($C_5H_{11}.C_5H_9O_2$)	...	...	...	...	...	10	...	10	...	...	...	...	...	...
Tartaric acid (In cold saturated alcoholic solution)	...	...	...	...	...	10	...	...	...	5	5	5	...	...
Oxalic acid (In cold saturated alcoholic solution)	...	1	...	...	1	...	...	1	...	...	...	...	...	...
Succinic acid (In cold saturated alcoholic solution)	...	...	...	...	...	1	...	...	3	1	1	...	...	...
Benzoic acid (In cold saturated alcoholic solution)	...	...	...	1	2	...	...	...	...	1	...	...	...	...

For full Tables of the British and Metrical Systems of Weights and Measures, the Percentage of Alcohol in Solutions of various Densities, etc., etc., see Author's "Analytical Chemistry."

APPENDIX B.

TABLE SHOWING THE RELATION BETWEEN THE DENSITY AND FLASHING POINT OF PARAFFIN OILS.

Specific Gravity of Paraffin Oil.	Flashing Point.	Specific Gravity of Paraffin Oil.	Flashing Point.
0·685	− 21°C. − 5·8°F	0·783	+ 50°C. + 122°F.
0·700	− 19° − 2·1°	0·792	75° 167°
0·740	+ 15° + 59·0°	0·805	90° 194°
0·750	17° 62·6°	0·822	110° 230°
0·760	35° 95·0°	Crude Petroleum.	
0·775	45° 113·0°	0·802	− 15° + 5°

FINIS.

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(Practical and Analytical).

ARRANGED ON THE PRINCIPLE OF

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SOUTH LONDON SCHOOL OF PHARMACY.

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ERRATA.

Page 17, line 12, *for* $\frac{273 \times 765 \times 265 \cdot 4}{(273 \times 140) \times 760,} =$ *read* $\frac{273 \times 765 \times 265 \cdot 4}{(273 + 140) \times 760} =$

" 19, " 3, " affected by dialysis, *read* effected by dialysis.

" 29, line 12, *for* soluble in excess, *read* insoluble in excess.

" 44, " 9, " $NH_4C_2O_4$, *read* $(NH_4)_2C_2O_4$.

" 47, " 12, " $H_2C_2H_4O_6$, *read* $H_2C_4H_4O_6$.

" 63, section 36, *for* hallogens, *read* halogens.

" 66, line 12, *for* HgCy, *read* $HgCy_2$.

" 68, 12 from bottom, *for* NH_4MoO_4, *read* $(NH_4)_2MoO_4$.

" 70, line 13, *for* NH_4MoO_4, *read* $(NH_4)_2MoO_4$.

" 71, " 5, " NHCl, *read* NH_4Cl.

" 77, 9 from bottom, *for* Sr or K, *read* Sr or Ca.

" 87, line 1, *for* red, *read* yellow.

" 104, " 9, " hypophosphate, *read* hypophosphite.

" 118, 2nd column, 5 from bottom, *for* white = Ph, *read* white = Pb.

" 135, line 15, *for* alicylate, *read* Salicylate.

" 155, " 20, " ·1855 *read* ·1895.

" 168, lines 15 and 23, *for* 416 *read* 420.

" " " 16 and 24, *for* 464 and 512, *read* 468 and 516.

N.B.—Students are advised to correct the above-mentioned typographical errors with pen and ink before commencing to read this book.

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CHAPTER I.

THE PROCESSES EMPLOYED BY PRACTICAL CHEMISTS.

It is advisable that the student should understand the *raison d'être* of the chief processes he will be called upon to employ, before commencing in detail the study of Analysis.

I. SOLUTION.

This process consists in stirring a solid body in contact with a fluid until it dissolves, heat being occasionally used. Bodies which refuse to dissolve in any particular fluid are said to be **insoluble** in it; the liquid used is called the **solvent**, and sometimes the **menstruum**; a liquid having taken up all the solid matter possible, is said to be **saturated**. A knowledge of the solubility of various substances in the chief menstrua, such as water, acids, alkalies, alcohol, ether, chloroform, and glycerin, is of the utmost importance both to the practical pharmacist and the chemist. By such knowledge we are enabled to separate one body from another; and by attention to minute details it is even possible to divorce bodies which are soluble in the same menstruum, but in different degrees. As an example we shall suppose three substances, one readily soluble, one partially so, and one but slightly soluble, in ether. By a careful use of three separate quantities of the liquid at different temperatures, we can obtain solutions of all three. This process is named *fractional solution*, and is so frequently employed in the manipulation of fatty substances, that the necessity of a thorough acquaintance with the relative solubility of bodies cannot be too strongly urged. In order to ascertain if any substance be soluble in any particular liquid, it is simply requisite to stir it into the fluid, applying heat if necessary. A portion of the liquid is then poured off, and heated until it has passed away in vapour, when, if any of the solid was held in solution, it will remain as a visible residue. As a general rule, the higher the temperature to which a liquid is raised, the greater becomes its capacity for saturation. Thus, one part of common nitre will require for solution about four parts of cold water; but the same weight of the solid will dissolve in less than half a part of boiling water. There are many exceptions to this rule, notably that of calcium oxide, which is less soluble in boiling water than in cold. If lime-water be saturated at 32° F., it will, on being raised to 212°, deposit about half its lime. It would appear, indeed, that all bodies have a particular temperature at which their solubility in certain fluids attains its *maximum*, and that with most substances such maximum is over 212°. Sodium sulphate, however, attains its maximum solubility in water at 60°; but as the temperature increases, its solubility decreases, so that at 212° and 32° it is almost equal. Many bodies, during solution, absorb so much heat that any substance placed in the liquid has its temperature remarkably reduced. Potassium nitrate and ammonium chloride, dissolved together in water, form in this manner a very efficient refrigerant when snow or ice are not attainable.

II. LIXIVIATION

Is the digestion of a mixture of solids in a fluid, so as to dissolve the soluble portion. Its accomplishment is very simple. The solids, in the form of powder, are introduced into a vessel, and the water or other liquid having been added, the whole is well stirred. Remaining at rest until all the insoluble matter has subsided, the clear fluid, charged with all that was soluble in the mixture, is decanted, or poured off. On the large scale, in chemical works, the clear liquor is usually drawn off by means of a **siphon**, which may be described as a bent tube having one limb longer than the other. It is filled with the liquid requiring removal, and the longer end having been closed by the finger or a tap arranged on purpose, the shorter limb is plunged nearly to the bottom of the clear fluid to be drawn off. On the tap being opened or the finger removed, an immediate stream issues from the longer limb, and continues to flow until the liquid has either been drained to below the level of the shorter limb, or the fluid in the receptacle supplied by the longer limb has attained the same level as that in the vessel which is being emptied. Why this should occur may be explained as follows:—The instrument commences to act by virtue of the increased weight of fluid in the longer limb, and once the motion so begins, it is perpetuated by the force of **cohesion** acting between the particles of the liquid. This may be familiarly illustrated by supposing a great weight of chain on the deck of a vessel, and when one end is thrown out over a roller fixed in the bulwarks sufficiently far to start the motion, the chain continues to run out until the whole is removed from the deck, however heavy the mass may have been.

III. PRECIPITATION

Is the mixing of two substances in solution so as to form a third substance, which, being insoluble in the fluids employed, sinks to the bottom, and is called the **precipitate**. The clear liquid which remains after the precipitate has settled down, is called the **supernatant liquid**.

When precipitates are totally insoluble in water, such as barium sulphate, or argentic chloride, the operation is best conducted at a boiling heat, as the high temperature causes the precipitate to aggregate and become more dense, so that it subsides rapidly, and is less liable to pass through the pores of a filter. Other precipitates, which do not form completely and instantaneously, and which are not absolutely insoluble in boiling water, are better treated by being allowed to digest for several hours at a gentle heat. Amongst these may be noted calcium oxalate. On the other hand, there are some precipitates which must never be heated, but be allowed to form slowly by standing in the cold for several hours. To this class belong ammonium-magnesium phosphate, and potassium acid tartrate. When it is desirable in qualitative analysis to cause such precipitates to form quickly, resort may be had to violent shaking, or stirring with a glass rod, so that it scrapes against the sides of the vessel. Precipitates are separated from the supernatant liquor by one of two methods. First:—

IV. DECANTATION,

Which consists in allowing the precipitate to settle to the bottom of the liquid; pouring off the clear liquor, then pouring on distilled water, and repeating the process until the precipitate is thoroughly washed. Second:—

V. FILTRATION,

Which consists in transferring the whole to a piece of folded paper or cloth, so that the liquid passes through, while the precipitate remains. This may be washed by the addition of distilled water. The liquor which has thus passed through the filter is called the **filtrate.** The process of precipitation is probably one of the most common with which the practical pharmacist meets in manufacturing the various chemicals in which he deals, or that he is called upon to analyze; and a knowledge of the exact quantities of the substances necessary to produce a given weight of precipitate desired, or, conversely, the weight of precipitate which a given quantity of any two substances will produce, is of the highest importance. Full instructions for such calculations are found in Chap. I., Part I.

VI. THE MEASUREMENT OF HEAT.

The ordinary **thermometer** for measuring heat is a graduated vacuous glass tube containing mercury. It is thus constructed:—A tube of glass about a foot long, having a small and uniform bore, is selected, and one end is, by the aid of the blowpipe, closed and expanded into a bulb. This is cautiously heated in order to drive out a portion of the air, when the open end of the tube is immediately dipped into a cup of mercury, some of which rises into the bulb as the latter cools. Once more applying heat, the mercury is made to boil, and the remaining air is replaced by mercurial vapour. Again the open end is plunged in the vessel of mercury, and on cooling more mercury is sucked up. This operation is repeated until a sufficient quantity of mercury has been got into the tube, so that it fills the bulb, and stands, when cold, a few inches up the tube. The working part of the instrument is now nearly complete, and it only requires hermetically sealing to be finished. To accomplish this, the open end of the tube is carefully heated, and a part of it drawn out, so that its diameter is reduced to about one-tenth; the bulb is then heated until the metallic column rises above this reduced bore, when the application of the blowpipe flame fuses and closes the tube, and the mercury on cooling sinks back to its original level, leaving a vacuum in the upper part of the tube. The instrument is now ready for graduation, which is done by first plunging the bulb into boiling water or exposing it to the steam arising therefrom, when the point reached by the mercury after repeated experiments is noted, and a scratch made with a diamond or file. The same operation is then pursued with melting ice, and the point at which the mercury ceases to sink is noted, and marked as before. Thus, two exact and undoubted indications of heat extremes, namely, the freezing and boiling points of water, being secured and marked, the subdivision of the scale into degrees and fractions is easily managed.

There are three systems on which this may be carried out:—(1) **Fahrenheit,** by which the distance between the two fixed points is measured off and carefully **divided into 180 equal degrees.** (2) **Celsius,** or **centigrade,** by which the same distance is **divided into 100 degrees.** And (3) **Réaumur,** by which the distance is **divided into 80 degrees.** It is important for the purposes of calculation to remember that the space occupied by 180 F. degrees is exactly the same as that covered by 100 C. and 80 R. respectively; or, taking the simplest arithmetical ratio, we have 9 degrees F. being exactly as long as 5 C. and 4 R. Having thus obtained the value of a degree, it is evident a scale may be made of any length; but it is of course needless to go lower than the freezing, or higher than the boiling, point of mercury, as it is only between these two extremes that a mercurial thermometer would be of any

use. The following shows the extreme possible scale that can be put on such instruments by each system :—

	Fahrenheit.	Celsius.	Réaumur.
Mercury boils	662	350	280
Water boils	212	100	80
Water freezes	32	0	0
	0	−17·7	−14·2
Mercury freezes	−40	−40	−32

In attaching the scales, the F. one is placed with 32 opposite the water-freezing scratch, and then, if the scale be correctly made, 212° will coincide with the boiling scratch; but in the cases of C. and R., the zeros are placed at the freezing point, and the boiling points then coincide with 100° C. and 80° R. respectively.

It is to be deplored that the chemists of all countries have not decided on the universal employment of one style of graduation for thermometers, as such an agreement between them would tend to vastly simplify calculations, or at least to diminish their extent. Fortunately, however, the change from one scale to another is not very difficult; and as it is of importance to be able to translate the indications of any thermometer into the scale of the one in use, the following directions are offered.

1. To convert degrees of **Centigrade** into degrees of **Fahrenheit**; multiply by 9, divide by 5, and add 32.
2. From **Fahrenheit** to **Centigrade**; deduct 32, multiply by 5, and divide by 9.
3. From **Réaumur** to **Fahrenheit**; multiply by 9, divide by 4, and add 32.
4. From **Fahrenheit** to **Réaumur**; deduct 32, multiply by 4, and divide by 9.
5. From **Centigrade** into **Réaumur**; multiply by 4, and divide by 5.
6. From **Réaumur** to **Centigrade**; multiply by 5, and divide by 4.
7. Degrees of frost **Fahrenheit** (between 32° and 0) into **Centigrade** or **Réaumur**; deduct from 32, then multiply by 5 or 4 respectively, and divide by 9, and put a minus sign before the answer.
8. Degrees below zero **Centigrade** and **Réaumur** (but still above −17·7 and −14·2 respectively) into degrees **Fahrenheit**; multiply by 9, and then divide by 5 or 4 respectively, and deduct the result from 32.
9. Degrees below 0 **Fahrenheit** into **Centigrade** or **Réaumur**; add 32, then multiply by 5 or 4 respectively, divide by 9, and put a minus sign before the answer.
10. Degrees **Centigrade** and **Réaumur** (below −17·7 and −14·2 respectively) into degrees **Fahrenheit**; multiply by 9, and divide by 5 or 4, as the case may be, deduct 32 from the answer, and put a minus sign before the difference.

Thermometers intended for extremely low temperatures are filled with coloured alcohol. They may be used for almost any attainable cold, but are not available above 173° Fah., at which point alcohol boils. For heats above the boiling point of mercury, an instrument called the **pyrometer** is employed.

It is in its simplest form a bar of platinum, fixed at one end, and acting on an index at the other. When the bar is heated, it expands and pushes forward the loose end, which causes the index to move. Another form is a bulb and tube of platinum, filled with air, placed in the furnace, and connected outside with a U tube containing mercury. The expansion of the air acting on the mercury drives it upwards, and indicates the temperature. **Maximum** and **minimum** thermometers are furnished with a small index inside the tube, so constructed that it remains at the highest or lowest point respectively touched by the fluid since the instruments were set.

However useful the thermometer may be for ordinary purposes, a state of heat exists which is not appreciable by that instrument, and requires to be measured in a totally different way. For example:—When once a liquid (say water) reaches the boiling point, its temperature remains stationary, provided the operation be conducted in an open vessel. The furnace underneath may be urged by any and every means known to science, and an immense amount of heat may pass into the liquid, and yet this excess of caloric remains unregistered by the thermometer. The heat thus apparently lost is called **latent heat**, and is necessary for the retention of the fluid in a state of vapour. Thus we see that vapours are only the corresponding fluids plus latent heat. All fluids are also only the corresponding solids, plus an amount of latent heat; because we find that if we take a pound of water at 32° (0° C.) and a pound of water at 174° (79° C.), and mix them, we shall produce two pounds of water having a temperature of 103° (39·5° C.). But if we mix a pound of ice at 32° (0° C.), with one pound of water at 174° (79° C.), and examine the mixture at the moment that the melting of the ice is complete, we shall find that the temperature of the resulting two pounds of water will be 32° (0° C.); in other words, that the pound of water has lost 174° (79° C.) of heat in melting the pound of ice.

The heat thus rendered inappreciable by the thermometer during the change from a solid to a liquid is called the *latent* heat of fusion. It is estimated by means of an instrument called the **calorimeter** (the description of which will be found in any book on physics), and is expressed in **thermal units**.

A thermal unit is the amount of heat required to raise one gramme, one kilogramme, or one pound, of water from 0° C. to 1° C. Either of these units may be employed, but the most generally recognised is the gramme. In the above example, we found that a pound of ice in melting would cool a pound of water through 79° C.; and we therefore say the latent heat of fusion of ice is 79 thermal units.

The reason why water should be taken as a standard is found in this result, it being the highest of all bodies as regards latent heat. To give some idea of how bodies vary in this respect, it may be mentioned that the latent heat of fusion of silver is 21, of tin 14, and of lead 5·4 thermal units.

The heat masked when a liquid changes into a gas is called the latent heat of vaporization. It is made manifest in the ordinary process of distillation, and so great is it in the case of steam, that one pound of water boiled and the steam therefrom passed through a worm surrounded by 5·36 pounds of water at the freezing point, will actually bring the whole contents of the condenser to 100° C. at the moment when the whole has passed away. Going upon this experiment, we therefore consider the latent heat of steam to be 536 thermal units.

Freezing mixtures depend for their action on latent heat. A mixture of ice and salt, for example, melts so rapidly, and consequently abstracts heat from the surrounding bodies so completely, as to produce a degree of cold considerably below the freezing point of water. Besides this simple mixture, we have ammonium chloride and ammonium nitrate, and, a more energetic

mixture of snow and crystallized calcium chloride, which is powerful enough to freeze mercury. The most powerful freezing mixture known, is that of carbon disulphide and liquid nitrous anhydride, which produces a cold of $-140°$ C.

VII. DISTILLATION

Is the changing of a fluid into vapour by the aid of heat, and passing the vapour into a cooling apparatus, called the **condenser**, where, its latent heat being abstracted, it is again deposited as a liquid. This process is employed for the separation of volatile fluids from non-volatile substances. The fluid which passes over and is condensed in the receiver is called the **distillate**; while the non-volatile matter which remains in the retort is called the **residue**. By careful attention to their boiling points, various volatile fluids may thus be separated from each other. Suppose, for example, that we have a mixture of three substances boiling respectively at 180°, 220°, and 240°, and their separation is desired, we should introduce the mixture into a retort fitted with a thermometer, the bulb of which was placed just above the level of the fluid. The whole being then attached to the condenser, the heat would be gradually raised until the thermometer marked a little over 180°, when that temperature would be steadily maintained as long as anything continued to collect in the receiver. When the liquid ceased to accumulate, the receiver would be changed, and the temperature raised to a little over 220°, and the distillation continued until the second liquid had ceased to pass over. The receiver being once more changed, the heat would be again raised, and maintained until the last liquid had been obtained as a distillate. This process, which is exceedingly useful in practical Chemistry, is called **fractional distillation.**

VIII. SUBLIMATION

Is the changing of a solid into a vapour by heat, and recondensing the vapour into a solid form in a cooled vessel. It is employed for the separation of volatile from non-volatile solids, and is thus conducted :—The substance to be sublimed is thinly spread over the bottom of a shallow iron pan, and the vessel is covered with a sheet of bibulous paper perforated with numerous pin-holes or with a piece of muslin. By means of a sand bath, the heat is slowly raised to the desired degree, when the vapour passes through the strainer, and condenses in a cap of wood or porcelain, lined with stout cartridge paper, and placed over the heating-pan and kept cool. **Fractional sublimation** is often useful, and may be employed in a similar manner to fractional distillation.

IX. FUSION

Is the heating of a solid until it melts. It is usually carried out in a vessel called a "crucible," made of fire-clay. On the small scale, or for the purposes of analysis, fusion is generally conducted in porcelain crucibles; or, where the substances are such as would attack porcelain, in vessels of platinum or silver. Alkalies should be fused only in crucibles made of the latter metal. A peculiar kind of fusion, called **cupellation**, is resorted to in the assay of gold and precious metals. The impure gold is wrapped in a piece of lead foil, and the whole is then heated in a little cup made of bone earth called a **cupel**, when the lead and all impurities fuse and sink into the substance of the porous vessel, leaving the pure gold as a metallic button, which may then be weighed.

X. EVAPORATION

Consists in heating a fluid until the whole, or as much of it as may be required, passes off in vapour. A solution thus treated until it has wholly passed into vapour, is said to be **evaporated to dryness,** and the solid substance remaining is called the **residue.**

Solutions which contain any organic or volatile matter ought always to be evaporated on a water bath; that is, in a vessel exposed only to the heat of boiling water. With ordinary non-volatile or metallic substances in solution this precaution is unnecessary, and of no practical advantage. Evaporation may be conducted slowly, without raising the fluid to its boiling point, when it is called simple **vaporization**; but when sufficient heat is applied, the evaporation takes place rapidly, and is accompanied by the disengagement of bubbles of vapour, and the fluid is then said to be in a state of **ebullition.** All liquids possess the continual desire, as it were, to pass into vapour; and the amount of elastic force which the vapour thus given off exerts is called its **tension.** The more the liquid is heated, the greater becomes its tendency to vaporize, and consequently the more powerful is the tension of its vapour; and when the latter is sufficiently marked to overcome the pressure exerted by the atmosphere and the cohesion of the liquid itself, ebullition takes place. The boiling point of a fluid is therefore *the temperature at which the tension of its vapour is equal to that of the superincumbent atmosphere.* If the pressure of the atmosphere be increased artificially, the boiling point of the liquid will rise in proportion. For example: boiling water in an open vessel under ordinary circumstances will have a temperature of 212°; but water in a steam boiler, under a pressure of 60 lbs. per square inch, will be found to be heated nearly to 264°. As steam under pressure can thus be obtained at high temperatures, it is made use of for the rapid evaporation of liquids on a large scale, by causing it to pass into a jacket or through a coil of pipes surrounding the evaporating pan. The apparatus thus made use of is called a *steam bath,* the heat of which, according to the B.P., should be about 230° Fahr.

The boiling point of liquids is very variable, as will be seen from the following table:—

	FAHRENHEIT.	CENTIGRADE.
Ether, pure	95°	35°
„ (B.P.)	105	40·5
Chloroform	142	61
Alcohol, rectified spirit, 84 per cent.	175	79·5
„ proof „ 49 „	178·5	81·4
Water, barom. press. at 29·92 inches	**212**	**100**
Strong Sulphuric Acid	620	327
Mercury	662	350

If water be boiled in a chemically clean glass vessel, and more particularly if a precipitate be suspended in the water, the boiling does not take place regularly, but the liquid becomes heated above its boiling point, and suddenly rushes into vapour in gusts. This is called by practical chemists "bumping," and may be prevented by putting in a few fragments of platinum foil, which act as *nuclei,* to aid in the regular disengagement of the vapour.

XI. WEIGHING AND MEASURING.

Weight is caused by the attraction all bodies have for each other, which is known as gravitation. This attraction is exercised in proportion to the mass of matter existing in the bodies, and in inverse proportion to the square of the distance between them. As the earth is the largest body within our atmosphere, it follows that its attraction is always greater than that of any

surrounding matter; and the exercise of this excess of gravitation to the earth's surface is the cause of weight. Weighing is performed by means of the well-known appliance called the balance, aided by weights made either according to the English or the metrical system.

In the English weights of precision, any amount above 10 grains is usually represented by a series of small brass cylinders, from 10 to 1000 grains; then follow 6, 3, 3, 2 and 1 grains in platinum wire, and afterwards ·6, ·3, ·3, ·2 and ·1 of a grain in platinum, or, more frequently, in aluminium wire. Quantities of less than $\frac{1}{10}$ grain are weighed by a small rider of gold wire placed on the beam of the balance. The foundation of the English system is the inch, which is the $\frac{1}{39}$ part (nearly) of the length of a pendulum vibrating seconds of mean time in a vacuum at the level of the sea, and in the latitude of London: (the actual length of the pendulum is 39·1393 inches). One cubic inch of distilled water, measured at 60° F. and 30 inches barometrical pressure, weighs 252·45 grains, or 252½ grains nearly. There are 437·5 grains in an ounce, and 16 ounces (or 7000 grains) in a pound. Measure of capacity is obtained by weighing out 10 lbs. of water at 60° Fahr. and 30 inches bar., when the whole measures one gallon. The gallon is in turn divided into 8 pints (= 20 ounces, or 8750 grains of water, per pint); the pint into 20 fluid ounces (= 437·5 grains of water per fluid ounce); the fluid ounce is divided into 8 fluid drachms (= 54·68 grains of water per fluid drachm); and, lastly, the fluid drachm is divided into 60 minims (= ·91 grain of water in each minim).

In the metrical weights of precision those above one gramme are in brass; and then we have ·6, ·3, ·3, ·2, ·1, and following them ·06, ·03, ·03, ·02, ·01 all in platinum wire or thin foil. The quantities below ·01 (one centigramme) are weighed by a rider on the beam. The combination of 6, 3, 3, 2 and 1 have been chosen because they have been found to give the greatest number of possible combinations with the fewest weights. The metrical system is founded upon the *mètre*, which is theoretically equal in length to the ten-millionth part of a quarter of the meridian of the earth. The metre is multiplied and divided entirely by 10, thus :—

Kilo-metre	1000·
Hecto-metre	100·
Deca-metre	10·
Metre	**1·**
Deci-metre	·1
Centi-metre	·01
Milli-metre	·001

The metre taking the practical place of the English yard, the decimetre consequently takes the place of the foot, and the centimetre of the inch; and just as weight is got in our system from the cubic inch, so it is got metrically from the cubic centimetre, only much more simply, because 1 *cubic centimetre of distilled water, measured at* 4° C. *and* 760 *millimetres bar., weighs one gramme.* The gramme is multiplied and divided exactly as the metre; and measure of capacity is got from the fact that 1 kilogramme (1000 grammes) of water measures 1 litre, which becomes in turn the unit of capacity thus :—

WEIGHT.	CAPACITY.	NO. OF UNITS.
Kilo-gramme . .	Kilo-litre . .	1000·
Hecto-gramme . .	Hecto-litre . .	100·
Deca-gramme . .	Deca-litre . .	10·
Gramme	**Litre**	**1·**
Deci-gramme . .	Deci-litre . .	·1
Centi-gramme . .	Centi-litre . .	·01
Milli-gramme . .	Milli-litre . .	·001

So we see that using water at 4° C., a gramme by weight and a cubic centimetre or a millilitre by measure amount to the same thing; as likewise do a kilogramme by weight and a cubic decimetre or a litre by measure. The relation between the two systems is easily calculated from the following standards:—

METRICAL.	ENGLISH.
1 Gramme	= 15·432 grains
1 Kilogramme	= 2·205 lbs. (or 15432 grains).
1 Litre	= 1·76 pints (or 35 fl. oz. 2 drachms & 11 minims).
1 Metre	= 39·37 inches.

So that 1 decimetre is, as nearly as possible, 4 inches; and 1 decilitre, a trifle over $3\frac{1}{2}$ fluid ounces. [FOR FULL TABLES OF BOTH SYSTEMS, SEE THE APPENDIX; AND FOR FURTHER PRACTICAL INSTRUCTION IN WEIGHING AND MEASURING, SEE QUANTITATIVE ANALYSIS.]

XII. SPECIFIC GRAVITY

May be generally explained to be the weight of anything as compared with that of an equal volume of distilled water at a temperature of 60°. An acquaintance with the various cases which may occur in the taking of specific gravity is of great importance to the pharmacist, as it forms an exceedingly ready method of testing the purity and strength of many substances. A knowledge of the specific gravity of the various bodies in which he deals, also enables the pharmacist to tell at once what any given volume of a liquid ought to weigh, or conversely, what size of a vessel will be required to contain any given weight. The following are the chief varieties of cases which may occur in connection with practically testing the specific gravity of liquids and solids:—

CASE 1. **To take the specific gravity of a fluid.**—A small bottle of thin glass is procured, and carefully counterpoised upon a balance. It is then filled with pure distilled water at 60° F., and the weight of the water thus introduced accurately noted. The bottle, having been emptied and dried, is filled with the liquid to be tested, also at 60° F., and the whole is again weighed. By this means, having ascertained the weight of equal bulks of water and fluid, it only remains to divide the weight of the fluid by the weight of the water, and the product will be the specific gravity required. To make the calculation clear, observe the following examples:—

A counterpoised bottle filled with distilled water weighs 1000 grains; the same bottle filled with sulphuric acid weighs 1843 grains, then:—

$$\frac{1843}{1000} = 1{\cdot}843, \text{ the specific gravity of the acid.}$$

Again, the same bottle, carefully washed, and filled with rectified spirit, weighs 838 grains, then

$$\frac{838}{1000} = {\cdot}838, \text{ the specific gravity of rectified spirit.}$$

In practice, bottles are sold with little perforated stoppers, which, when entirely filled with the liquid, and the stopper carefully dropped in, so that no bubbles of air are allowed to remain between the stopper and the liquid, exactly hold a given weight of water, usually 1000 grains. A counterpoising weight for the empty bottle is also provided; so that there is nothing further to be done but simply to place the counterpoise in one scale and the bottle, filled with the liquid under examination, in the other; and having ascertained the weight, to divide by the known weight of water for which the bottle was constructed.

To take the specific gravity of a liquid by means of the hydrometer.—The hydrometer depends for its action on the theorem of Archimedes. If a solid

body be immersed in a liquid specifically heavier than itself, it continues to sink until it has displaced a bulk of fluid equal to its own weight, and then it becomes stationary. Suppose an elongated body with a weight at its base to cause it to float upright, which has a specific weight exactly half that of water, be immersed in that fluid; it will sink to exactly half its length, because its whole weight is counterpoised by a bulk of fluid equal to half its size. Hydrometers are long narrow glass or metal tubes with a bulb near the bottom filled with air, and another smaller bulb beneath containing a sufficient quantity of mercury to weight it and cause it to float upright. There are two kinds of hydrometers: (1) for fluids heavier than water, and (2) for fluids lighter than water. The graduation of the former is performed by immersing the instrument in water and introducing such a quantity of mercury as will cause it to sink, so that only about one inch remains unsubmerged, and marking this point 1. The instrument is then plunged successively into several liquids heavier than water, the specific gravities of which are known, and the points to which it rises are marked and numbered. By this means a scale can be made between those points, indicating any gravity from 1 upwards. For hydrometers lighter than water, the first sinking in that liquid is continued by weighting until only the upper bulb is immersed; and this point having been marked 1, the instrument is placed successively in known fluids lighter than water, the points to which it sinks marked, and by this means a whole scale is obtained. The hydrometers sold for B.P. purposes are generally four in number, the first ranging from ·70 to 1·00, the second from 1·00 to 1·30, the third from 1·30 to 1·60, and the fourth from 1·60 to 2·00. Such a set will take the gravity of any B.P. liquid except the exceptionally heavy liquor hydrargyri nitratis acidus, which has a gravity of 2·246. The following is a table of the specific gravities of the chief B.P. liquids.

1. Fluids lighter than Water.

Æther purus	·720	Spiritus chloroformi	·871
Æther	·735	Liquor ammoniæ fortior	·891
Spiritus ætheris	·809	Spiritus tenuior	·920
Alcohol amylicum	·818	Acidum sulphuricum aromat.	·927
Spiritus rectificatus	·838	,, hydrocyanicum dil.	·997
,, ætheris nitrosi	·845	Tinctura ferri perchloridi	·992
,, ammoniæ aromaticus	·870		

2. Fluids heavier than Water.

Acidum aceticum dil.	1·006	Liquor hydrargyri nitratis acidus	2·246
,, ,, glaciale	1·066	,, plumbi subacetatis	1·260
,, carbolicum	1·065	,, potassæ	1·058
,, hydrochloricum	1·160	,, sodæ	1·047
,, ,, dil.	1·052	,, ,, chloratæ	1·103
,, nitricum	1·420	Syrupus simplex	1·330
,, ,, dil.	1·101	,, aurantii	1·330
,, nitro-hydrochloricum dil.	1·075	,, ferri iodidi	1·385
,, sulphuricum	1·843	,, hemidesmi	1·335
,, ,, dil.	1·094	,, limonis	1·340
,, sulphurosum	1·040	,, mori	1·330
Extractum cinchonæ flavæ liq.	1·100	,, papaveris	1·320
,, sarzæ liq.	1·130	,, rhœados	1·330
Liquor antimonii chloridi	1·470	,, rhamni	1·320
,, arsenicalis	1·009	,, rosæ Gallicæ	1·335
,, arsenici hydrochloricus	1·009	,, sennæ	1·310
,, bismuthi et ammoniæ citratis	1·122	,, tolutanus	1·330
,, calcis chloratæ	1·035	Bromine	2·966
,, ,, saccharatus	1·052	Chloroform	1·490
,, chlori	1·003	Creasote	1·071
,, ferri perchloridi	1·338	Glycerin	1·250
,, ,, pernitratis	1·107	Vinegar	1·017 to 1·019
,, ,, persulphatis	1·441		

By Act of Parliament Sykes' hydrometer is used by the officers of excise to indicate the strength of spirituous liquors, and thus facilitate the collection of the revenue. It is a short brass instrument with the stem graduated from 0 to 10, and a series of nine weights to place beneath the bulb. By thus being able to change the weight, the length of the stem is only $\frac{1}{10}$ of that it would need to be with a permanent weight, and so the instrument will work in a proportionately smaller quantity of liquid. In using it, the thermometer must also be employed; and by observing (1) the temperature, (2) the weight put on, and (3) the point to which it sinks on the stem, and referring to a book of tables which is sold with the hydrometer, the strength of the spirit is ascertained.

Another modification of the instrument is found in Twaddell's hydrometer, which is used in this country for testing the density of liquids having a greater specific gravity than water. It is so graduated that the reading of any indicated degree, multiplied by 5 and added to 1000, gives the specific gravity as compared with water. Specific gravity beads form the only other variation of the hydrometric idea. These are small loaded bulbs of known specific gravities, which are thrown into the liquid to be tested, when the number marked upon the bead which just floats underneath the surface and shows no tendency to sink or rise, gives the specific gravity required. Hydrometers in any form must in accuracy rank considerably beneath that of the specific gravity bottle; but in commercial operations, where an approximation only to correctness is required, this little instrument is invaluable.

CASE 2 **To take the specific gravity of a solid body in mass which is insoluble in and heavier than water.**—The method by which this process is conducted was suggested by a theorem attributed to Archimedes, which may be thus expressed:—A solid on being immersed in a liquid is buoyed up in proportion to the weight of the fluid which it displaces, and the weight it thus apparently loses is equal to that of its own bulk of the liquid. A piece of the solid substance to be tested is accurately weighed, and is suspended by means of a horsehair from one arm of a balance so that it dips under the surface of a vessel containing distilled water at 60° F., when its weight is again noted. Its weight in water is deducted from its weight in air, the weight in air being divided by the difference so obtained.

EXAMPLE.

A piece of marble weighs	300 grains.
Immersed in distilled water. . . .	188·9 ,,
Difference in weight	111·1 ,,

By dividing 300 by 111·1 we obtain the product 2·7, which is the specific gravity of the marble.

CASE 3. **In order to arrive at the specific gravity of a powder which is insoluble in and heavier than water.**—Weigh a portion of the powder in air, then introduce it into a counterpoised specific gravity bottle constructed to hold a known weight of water. Let the bottle be carefully filled with distilled water, gently agitating to ensure that no minute bubbles of air shall remain attached to the particles of powder, then weigh the whole. From the weight of the powder in air, plus the known weight of water which the bottle should contain, deduct the weight obtained in the second operation, and divide the original weight of the powder by this difference.

EXAMPLE.—20 grains of a powder are weighed out, and poured into a counterpoised specific gravity bottle, constructed to hold 1000 grains of water. The bottle thus charged is found to weigh 1012 grains; then,

20 grains + 1000 grains	=	1020 grains.
Weight of the bottle when charged with powder and water. . .		1012 "
Difference		8 "

Therefore, 20 grains divided by 8 grains will give 2·5 as the specific gravity of the powder.

CASE 4. **To take the specific gravity of a substance in mass, insoluble in but lighter than water.**—The difficulty met with in this case consists in the impossibility of weighing such a substance alone in water, because it floats on the surface of that liquid. It therefore becomes necessary to attach a piece of lead or other solid sufficiently heavy to sink it, and thus a complication is introduced. The light substance is first weighed in air in the ordinary manner, and is then attached by a horsehair or silken thread to a sinker, and suspended from one arm of a balance under the surface of a basin of distilled water, when the combined weight of both is ascertained. The light body is now detached, and the weight of the heavy solid substance by itself noted. By these means we obtain the following data :—

i. The weight of the light body in air.
ii. The weight of the heavy body in water.
iii. The weight conjointly of the light body and sinker in water.

We then deduct the weight of both in water from the weight of the sinker in water; add the weight of the light substance in air; and divide the weight of the light body in air by the product so obtained.

EXAMPLE. A light substance weighs 120 grains in air; being attached to a piece of lead, and weighed in distilled water, the united weight amounts to 40 grains, while the weight of the lead alone in water shows 50 grains. Then :—

Weight of lead in water	50 grains.
Weight of both in water	40 "
Difference	10 "
Add weight of light body in air	120 "
Product	130 "

Dividing 120, the weight in air, by 130 obtained as above, we arrive at the decimal fraction ·923 as the specific gravity of the light substance tested.

CASE 5. **To obtain the specific gravity of a substance soluble in water.**—Proceed exactly in the same manner as in Cases 2 or 3, according as the body is in mass or in powder; but instead of water, use oil of turpentine or some other liquid in which the solid is insoluble. Having obtained the specific gravity of the substance as if water had been used, multiply the result by the known specific gravity of the oil of turpentine or other fluid employed.

EXAMPLE.—A lump of sugar weighing 100 grains was found to weigh when immersed in oil of turpentine, 45·62 grains. Then :—

The weight of the sugar in air was	100 grains.
" " oil of turpentine .	45·62
Difference	54·38

Dividing 100 grains by 54·38 grains yields 1·84 as the specific gravity as if water had been used; and by multiplying this result by ·87, the specific gravity of oil of turpentine, we obtain 1·6 as the actual specific gravity of the sample of sugar operated on.

Having thus considered in detail the various complications which may arise in taking the specific gravity of liquids and solids, it only remains to point out how the foregoing may be rendered subservient to commercial purposes.

CASE 1. **The specific gravity of a body being known, it is desired to ascertain the weight of any given volume of the substance.** In order to obtain an answer, it is simply necessary to discover what would be the weight of the given bulk considered as water, and to multiply this amount by the specific gravity.

EXAMPLE i.—What would be the weight of a fluid ounce of oil of vitriol? We know that a fluid ounce of distilled water weighs 437·5 grains, and in the Pharmacopœia the specific gravity of oil of vitriol is given as 1·843; so, if we multiply the former figures by the latter, we obtain 806·31 grains, which is the weight of a fluid ounce of this acid.

EXAMPLE ii.—How much should a gallon of *extractum cinchonæ flavæ liquidum* weigh? The weight of a gallon of water is 10 lbs., by multiplying 10 by 1·1, the specific gravity of the extract, we obtain 11 lbs. as an answer to the question.

EXAMPLE iii.—How much should a fluid ounce of pure ether weigh? The specific gravity of this exceedingly volatile fluid is ·72, and we have already seen that a fluid ounce of distilled water weighs 437·5 grains; multiplying the one number by the other gives 315 grains, which corresponds to the weight of a fluid ounce of the first-mentioned liquid.

CASE 2. **Given the weight of any known bulk of a liquid, to find its specific gravity.**—Divide the weight by that of the given bulk considered as distilled water.

EXAMPLE.—A pint of spirit weighs 7332 grains;—is it rectified or proof spirit? By dividing this weight by 8750, the ascertained weight of a pint of distilled water, we obtain as an answer ·838. We know, therefore, that the spirit thus tested must have been rectified and not proof, as the specific gravity of the latter would have shown ·92.

XIII. MEASUREMENT OF ATMOSPHERIC PRESSURE AND DENSITY OF GASES AND VAPOURS.

Taking the density of gases and vapours involves many more complicated considerations than are required in the methods applicable to the specific gravity of liquids and solids. The standard adopted for gases and vapours is hydrogen, measured at a temperature of 0° C., and a barometrical pressure of 760 millimetres. The observation of the temperature is accomplished by means of the thermometer already explained; whereas the pressure of the atmosphere is ascertained by the aid of an instrument named the **barometer.** A pupil of Galileo, named Torricelli, and others had previously remarked that water in an ordinary suction pump refused to follow the piston higher than about 33 feet. But whilst the savans of the period attributed this circumstance to "Nature's abhorrence of a vacuum," the eminent disciple of Galileo conceived that the effect was due to a limitation or counter-balancing of atmospheric pressure. Having thus advanced a stage in his chain of reasoning he concluded that if he employed a heavier fluid than water it would not rise so high in the tube as that liquid, but that its height would be in proportion to its specific gravity. Another link in the chain was now added, and his theory became complete when he argued that any liquid must rise in a sealed tube exhausted of air (having its open mouth dipping into a reservoir of the

same fluid) until its altitude corresponded with, and balanced the weight of the superincumbent atmosphere pressing on the surface of the liquid contained in the reservoir.

The barometer is constructed as follows :—The thick glass tube is sealed at one end, and rendered chemically clean. The mercury to be employed is purified by agitation with dilute sulphuric or nitric acid; kept under the cleansing liquid for several days, then washed with fresh acid, and its lustration completed with distilled water. The purified metal and tube being both perfectly dry, the former is poured into the latter to the height of about six inches and boiled for a few seconds. A further supply of separately heated mercury is added, and ebullition again induced as before. Alternately filling up gradually and boiling, the process advances, until the barometrical tube is full, and not a particle of air remains; in order to prevent subsequent fracture, the tube must be carefully annealed, that is, permitted slowly to cool. It is then simply to be closed with the finger, and inverted in a small vessel of mercury, taking great care that no bubbles of air pass in during the inversion. When this is done, the mercury sinks down from the top and stands at a height which balances the atmospheric pressure of the day, leaving above it a space known as the *Torricellian vacuum*. The instrument is then graduated in inches or millimetres from the surface of the mercury in the cup upwards. In practice, the graduation commences at 26 inches above the mercury surface, and ends at 32 inches, as the barometer never varies more than that. In millimetres likewise the graduation commences at 700 and ends at 800, for the same reason. The barometer is said to be at standard pressure when the column of mercury is 29·9 inches, or 760 millimetres long. A modern adaptation of the law of atmospheric pressure to the purposes of science is found in the **aneroid barometer**. It consists of a vacuous circular metal box, with a fluted lid, which is more or less affected by atmospheric changes, that is to say, when the pressure increases the lid is crushed inwards, and springs out again by its own elasticity, when the pressure diminishes. The atmospheric fluctuations are exhibited on a dial by an indicator placed in connection with the metallic moving surfaces. The instrument is graduated by placing alongside it a true mercurial barometer, and observing how far the index passes for each real rise or fall of the mercury. The aneroid, therefore, is only a true barometer when graduated thus side by side with a mercurial column.

The most convenient and widely recognised scales, both for the thermometer and barometer, are those employed on the Continent for the measurement of gases. Among scientific persons, whenever any volume of gas is mentioned, it is understood to have been measured at a temperature of zero as indicated by the Centigrade thermometer; and under a pressure equal to sustain a column of mercury 760 millimetres in height on the French barometer.

In the case of liquids or solids, when taking their specific gravity, it is not only possible but easy to obtain the water or other fluid required at the exact temperature necessary, by the use of cooling or heating appliances. With a gas we can exercise no such manipulation; and although we might control the temperature, we are absolutely powerless to influence the pressure of the atmosphere at the period of measurement. The measurement of gases is therefore conducted without any attempt to modify these conditions; but the indications of the thermometer and barometer being carefully noted at the time of the experiment, a simple series of calculations enables us to ascertain how much the volume of gas would have measured had the test been conducted at a standard of temperature and pressure. The following are specimens of such calculations :—

1. **Correction of the volume of gases for temperature.**—This calculation is based upon the discovery that gases expand or contract one two-hundred-and-seventy-third ($\frac{1}{273}$) part of their volume for each degree of temperature, Centigrade, through which their heat has been respectively raised or lowered. This fact, therefore, enables us, by a simple rule-of-three sum, to obtain the following result:—As 273 plus the temperature at the time of measurement is to 273 plus the required temperature, so is the volume of the gas at the period of measurement to the required volume.

For example:—the volume of a gas at 15° C. was 100 cubic centimetres, what would it be at the standard temperature at 0° C.? Then,—

$$\begin{array}{lrcrcr} \text{As} & 273 & & 273 & & \\ & 15 & & 0 & & \\ \hline & 288 & : & 273 & :: & 100 \end{array}$$

which gives, as an answer, 94·795 cubic centimetres, the volume of the gas at standard temperature.

2. **Correction of the volume of gases for pressure.**—This calculation is based upon the rule that gases expand or contract in volume in inverse proportion to the increase or diminution of the pressure: that is to say, the greater the pressure the less the volume of the gas, and the less the pressure the greater the volume of the gas.

For example:—At the moment of measuring 100 cubic centimetres of a gas, the barometer stood at 752 millimetres; what would the volume of the gas be at the standard pressure of 760 millimetres? Applying the rule of inverse proportion, we have the following simple directions for stating the sum:—As the required pressure is to the observed pressure, so is the observed volume to the required volume: then

$$760 \quad : \quad 752 \quad :: \quad 100$$

which gives, as an answer, 98·95, the volume of the gas at standard pressure.

The manner in which the specific gravity of a **permanent gas** is obtained is as follows:—

A sufficiently large globe of very thin glass is procured, fitted with a brass cap and a perfectly air-tight stopcock. Inside the globe, projecting from the cap, a small, delicate thermometer must be fixed for the registration of the temperature, and a barometer of known accuracy placed within sight of the manipulator, to indicate the atmospheric pressure. The gas to be tested must be generated at the time it is required, and passed without delay into the previously exhausted globe, through a considerable length of glass tube filled with some hygroscopic mixture, such as fragments of pumice stone moistened with sulphuric acid, so that during its passage it may be robbed of every trace of moisture. Some pressure being necessarily used in obtaining the gas, its elasticity when in the globe will, to a trivial extent, surpass the atmospheric pressure; but by opening the tap for an instant, an equilibrium is established, and the necessity for barometric correction sometimes avoided. The filled globe is now weighed, and its weight noted, together with the indication of the temperature shown by the little thermometer inside, and that of the barometer. Placed on the air-pump, the sphere is then carefully exhausted, detached, and the weight recorded. Finally, it is filled with pure, dry air, and once more tested by the balance, when, if the temperature and barometric pressure happen to be alike during all three weighings, the specific gravity required will be known by dividing the weight of the gas by that of the air.

The specific gravity of vapour is more difficult of attainment, and the process, which necessitates the most delicate manipulation, is as follows:— A thin, clean, dry, glass globe, about three inches in diameter, is employed, its neck is drawn out into a fine tube in the blow-pipe flame, and the vessel is accurately weighed, and the temperature and pressure at the moment accurately noted. By gently heating the bulb and dipping the attenuated opening into the volatile liquid whose vapour is to be weighed, a suitable quantity (say 100 grains) is driven into the globe by the pressure of the air. Attaching a handle by means of wire, the sphere is plunged into an oil bath, furnished with a thermometer, and is then heated somewhat above its volatilizing point. When all vapour has ceased to issue from the globe, the orifice is hermetically sealed, and the temperature and pressure again noted. The apparatus is allowed to cool, separated from the handle, cleansed, weighed, and the weight noted. The last step is to break off a fragment of the neck beneath the surface of a sufficiently large vessel of mercury, when, should the experiment have been carefully performed, the liquid enters the globe, completely filling it, and the capacity is ascertained by emptying its contents into a graduated glass measure. If any residual air remain in the globe, it must be also measured and subsequently allowed for, but, supposing the experiment to have been perfectly successful, we have the following five data:—

1. Weight of globe filled with air.
2. Temperature and pressure at the time of weighing.
3. Weight of globe, plus vapour.
4. Temperature and pressure at sealing.
5. Capacity of the globe.

Proceeding from these data, the first point is to find the actual weight of the globe. This is done by calculating the capacity of the globe from the temperature and pressure at the time of weighing to 0° C. and 760 mm. bar. and then multiplying the true volume thus found by ·001295, which is the weight of a cubic centimetre of air (1 litre at 0° C. and 760 mm. bar. = 1·295 gramme). Having thus obtained the weight of the air, it is deducted from the weight of globe and air, and the difference gives the true weight of the globe; and by deducting this latter from the weight of the globe plus vapour, we obtain the actual weight of the vapour. But as this weight is that of the volume of vapour at the temperature and pressure at the moment of sealing, it must be corrected to standard temperature and pressure, and the weight of an equal volume of hydrogen ascertained. To do this, the capacity of the globe is once more put down and reduced from the temperature and pressure at sealing to 0° C. and 760 mm. bar., and the resulting volume is multiplied by ·0000896 which is the weight of 1 cubic centimetre of hydrogen (1 litre at 0° C. and 760 mm. bar. = ·0896 gramme). The product, which gives the actual weight of an equivalent volume of hydrogen, is then taken and divided into the weight of the vapour already found, and the answer is the density. Taking for example an experiment on the vapour density of acetic acid, in which the data were:—

1. Weight of globe + air, 12·486 grammes.
2. Temp. and bar. at weighing, 15° C. and 765 mm. bar.
3. Temp. and bar. at sealing, 140° C. and 765 mm. bar.
4. Weight of globe + vapour, 12·632 grammes.
5. Capacity of globe, 265·4 cubic centimetres.

1. What would be the true volume at 0° C. and 760 mm. bar., of 265·4 cc., measured at 15° C. and 765 mm. bar?

$$\frac{273 \times 765 \times 265{\cdot}4}{(273 + 15) \times 760} = 253{\cdot}2 \text{ cc.}$$

2. What is the weight of 253·2 cc. of air, at 0° C. and 760 mm. bar.?

$$253{\cdot}2 \times {\cdot}001295 = {\cdot}328 \text{ gramme.}$$

3. Knowing now the actual weight of the air enclosed at the time of weighing was ·328, what was the true weight of the globe?

$$12{\cdot}486 - {\cdot}328 = 12{\cdot}158.$$

4. Knowing thus the true weight of the glass, what weight of vapour was in it at the moment of sealing?

$$12{\cdot}632 - 12{\cdot}158 = {\cdot}474 \text{ weight of vapour.}$$

5. At sealing we had 265·4 cc. of vapour at 140° C. and 765 mm. bar., how much would that be at 0° C. and 760 mm. bar.?

$$\frac{273 \times 765 \times 265{\cdot}4}{(273 + 140) \times 760} = 176{\cdot}6 \text{ cc.}$$

6. Knowing now the true amount of vapour in the globe, what would that volume weigh, if it had been hydrogen?

$$176{\cdot}6 \times {\cdot}0000896 = {\cdot}0158 \text{ gramme.}$$

7. But this volume of vapour really weighed ·474 gramme, therefore :—

$$\frac{{\cdot}474}{{\cdot}0158} = 30$$

and the vapour density of acetic acid is therefore 30.

XIV. CRYSTALLIZATION.

Many substances when dissolved in a boiling liquid separate out in masses as soon as the fluid cools. Such masses have a well-defined and symmetrical shape, bounded by plain surfaces and regular angles. These bodies are named **crystalline**; the deposited masses, **crystals**; and the remaining solution, the **mother liquor.** Substances which are not susceptible of crystallization are called **amorphous** (*i.e.*, formless) bodies; while solids, such as glue and gums, which are soluble in water and yet not crystallizable are named **colloids.** Crystallization may also occur during solidification after fusion, and by the spontaneous evaporation of liquids holding crystalline substances in solution. All crystalline bodies invariably assume the same form, and may thus be unmistakably recognised from each other. The process is also useful for purification, as at the moment of crystallization all impurities are rejected, and may be poured off with the mother liquor. Many circumstances affect the size of the crystals produced in any solution; as a rule, the more rapidly crystallization takes place, the smaller are the crystals. An example of the extreme variation in the size of the crystals produced from the same solution may be seen in ferrous sulphate. When allowed to deposit slowly, we have the ordinary well marked crystals of the *ferri sulphas* of the B.P.; but the same salt dissolved in boiling water, and the solution suddenly poured, with constant stirring, into spirit, gives the B.P. *ferri sulphas granulata*, whose crystals are so minute that a lens is required to distinguish them. For the formation of large and well defined crystals perfect rest is required, and it is often desirable to introduce pieces of wood or string so as to form nuclei on which the crystals collect. Good examples are seen in commercial crystallized sugar of milk and sugar-candy. Some bodies are capable of crystallizing in two or more forms, and are called **polymorphous.** A very interesting and

beautiful instance of this property may be seen in mercuric iodide, the *hydrargyri iodidum rubrum* of the B.P. As commonly sold, this is a red powder, and perfectly amorphous. If a little of it be heated, it becomes yellow, and when examined by means of a lens is found to consist of minute rhombic plates. Let it now be touched with a cold knife and its red colour will return, but instead of being amorphous, as it was originally, it exhibits a mass of diamond-shaped grains, called octahedra. Many substances on crystallizing combine with a certain amount of water, which would indeed appear to be necessary to their existence in the crystalline state. The water thus appropriated is named **water of crystallization**; it may be driven off by heat and the substance crumbles into amorphous powder. The colour of many crystalline bodies is also apparently dependent on the water of crystallization. Take a crystal of the well-known deep blue cupric sulphate, and heat it in a small porcelain crucible, when it will subside into a white powder entirely destitute of crystalline form. But on cooling, if a drop or two of water be added, the powder will immediately reassume its crystalline form, and regain its original blue colour. Early in the present century a relation called **isomorphism** was discovered to exist between crystalline form and chemical composition. Certain substances exist which resemble each other both in the shape of their crystals and in their general chemical composition, differing perhaps only in one ingredient. Such bodies are said to be **isomorphous** with each other. This relation is exemplified in magnesium, zinc, and ferrous sulphates, which when crystallized are alike in form, in the amount of water of crystallization, and in their general chemical constitution :—

Magnesium sulphate	$MgSO_4 7H_2O$.
Zinc sulphate	$ZnSO_4 7H_2O$.
Ferrous sulphate	$FeSO_4 7H_2O$.

All crystalline substances possess forms belonging to one of six chief systems. These systems are based upon the mutual relations of certain imaginary lines called *axes*, which are supposed to run through the body of the crystal, intersecting each other at its centre. These six systems of crystallization may be briefly mentioned.

1. **The regular, or cubic system,** in which the axes are all equal in length, and at right angles to each other. To this belong the cube (sodium chloride, potassium iodide, and potassium bromide); and the octohedron, including alum and the diamond.
2. **The square prismatic system,** in which the axes are also at right angles, but one is longer or shorter than the other two. Potassium ferrocyanide is an example.
3. **The hexagonal system,** having four axes, three equal in length, and in the same plane; and one unequal and at right angles to the other three. Examples: ice, sodium nitrate, and the mineral called quartz.
4. **The rhombic system,** in which there are three axes, all at right angles to each other, but all differing in length. Potassium nitrate is an example of this class.
5. **The monoclinic system** has three axes, all unequal, two being oblique while the third is at right angles to the plane of the other two. To this system belong sodium phosphate, sodium carbonate, cane-sugar, borax, and the isomorphous sulphates of zinc and magnesium as well as iron.
6. **The triclinic system,** in which the three axes are all different in length, and intersect each other obliquely. Cupric sulphate and potassium acid chromate are examples.

When small quantities of crystalline substances exist in a solution together with a large quantity of uncrystallizable colloid bodies, their mutual separation is affected by **dialysis.** This process consists in introducing the mixture into a glass vessel having a bottom made of vegetable parchment. This, called the **dialyzer,** is floated in a large quantity of distilled water in a basin. At the expiration of several hours the whole of the crystalline bodies will have passed through the parchment, and will have become dissolved in the water in the basin, while the colloids remain in the dialyzer. A very good way of practising this process is to dialyze a solution of glue in which a few grains of salt have been dissolved, when the salt will be found to have passed into the water in the basin, while all the glue will remain behind. This process is sometimes employed for the separation of crystalline poison, like strychnia, from the contents of a stomach.

XV. SPECTRUM ANALYSIS.

In describing this extremely delicate, and for many purposes exceedingly useful, method of analysis, it may be advantageous to give a few words of preliminary explanation. **Light** is, according to the modern theory, considered to be a series of undulations passing through space with immense rapidity, and acting upon the retina of the eye, but not necessarily upon the thermometer. These undulations always pass in straight lines, which are popularly known as **rays,** and the velocity of their passage is so great that light has been calculated to travel at the rate of 200,000 miles a second.

When a ray of light touches the boundary line between a rarer and a denser medium, such as the surface of a mirror, a part of it is thrown backwards at an angle equal to that at which it strikes the denser medium: this change in direction is called **reflection,** the law being stated as, that the angle of incidence is equal to the angle of reflection. Usually a portion of the ray is not reflected, but passes through the denser medium; although under some special circumstances the whole is thrown back.

Refraction is the change in direction which a ray of light undergoes on passing at an angle through a transparent medium denser than the air, the sides of which are parallel, such as a sheet of glass. When the ray falls upon the glass, it is bent from its course, and emerges from the other side of the glass in a line parallel to, but not continuous with, its original course. As a rule, the denser the medium the greater is the bending, or refraction, which the ray undergoes.

A **prism** is a triangular piece of glass, or other suitable transparent medium, which from the fact of its sides not being parallel, possesses the power of completely altering the direction of a ray of light, as well as bending it from its course. When a ray of sunlight is allowed to pass through a prism, it is thus deflected and *dispersed* into a number of rays differing in their degree of refrangibility. When these rays, as they pass from the prism, are caused to fall upon a white surface, they are observed to have a marked difference in colour. The image so produced is called a **spectrum**; and when sunlight is thus treated it is found to give a spectrum consisting of the following colours: viz., violet, indigo, blue, green, yellow, orange, and red, which may always be mechanically recollected by the word *vibgyor*.

The violet end of the spectrum, owing to its greater refrangibility, is always the nearer to the base or broad end of the prism.

By this means of separating the rays of light, we are able to ascertain the peculiar properties of each of the colours which go to compose it, and we find that the chemical activity of light resides chiefly in the most highly refrangi-

rays just outside the violet end of the visible spectrum, which are called the actinic rays; while on the other hand, the heat transmitted by the sun is most felt at the opposite or red end of the spectrum.

The actinic or chemical rays are those to which we are mainly indebted for many actions of chemical interest, such as the effect of the sun in photography, the formation of green colouring matter in plants, and the explosion of chlorine and hydrogen by sun-light. These rays may be rendered visible by passing them through a solution of quinine in dilute sulphuric acid, which possesses the property of causing the phenomenon of **fluorescence**, *i.e.*, the so lessening the refrangibility of the chemical rays as to render them visible as a pale blue sheen when the quinine solution is held up to the sunlight.

The invisible rays beyond the red end are entirely heat-giving. They are called the Herschellian rays, and may be separated by passing light through a prism of rock salt coated with iodine, which quite cuts off light and allows heat to pass. On the other hand a solution of alum cuts off heat, and transmits light. When the heat rays are allowed to fall on a piece of blackened platinum or charcoal *in vacuo* these bodies become heated to whiteness, thus exhibiting what is called **calorescence.**

Further research demonstrated, that if we substituted the light emitted from various bodies in a state of incandescence to the action of a prism, the image or spectrum produced varied in each case, and was, moreover, almost characteristic of the particular bodies employed. This discovery led to the invention of the spectroscope, which, in its simplest form, consists of a metallic diaphragm with a narrow slit, through which a ray of light from the burning body is allowed to pass and is condensed by a lens upon a prism of glass or, better still, a triangular bottle of thin glass filled with disulphide of carbon. At the opposite side of the prism is a short telescope, so arranged that an observer, looking through it, sees the spectrum or image produced by the light after passing through the prism.

When ordinary solar light is examined through the spectroscope, a number of dark lines are found crossing the image at certain fixed points. They are called "**Frauenhofer's lines**" and their position is characteristic of sunlight. It has been proved that such lines are only formed when the source of light contains volatile substances, as we find that the light emitted by a non-volatile heated body gives a continuous image devoid of lines. If, for example, a platinum wire be heated to a high temperature in a Bunsen burner, and the light thus produced be examined, no lines will be visible; but if the wire be now tipped with a fragment of sodium chloride, and once more ignited, a bright line will suddenly appear in the yellow of the spectrum, and in so dazzling a manner as to render the whole of the rest of the image almost invisible. In carrying out this system of analysis therefore, it is only necessary to procure a perfectly clean piece of platinum wire, with one end bent into the form of a loop, and place a Bunsen gas burner in such a position that the rays from anything heated in it will pass into the spectroscope. The wire is then to be moistened with a little hydrochloric acid, and having been dipped in the substance to be examined, is to be held in the hottest portion of the Bunsen flame, and its spectrum simultaneously observed through the spectroscope, noting carefully the colour, number, and position of the bright lines produced. When thus examined, we find that potassium exhibits one bright line in the red, and one in the blue; lithium, one bright line in the yellow, and one more brilliant in the red; strontium, one blue, one orange, and six red lines; barium, a number of lines chiefly green and yellow; calcium, three distinct bright yellow lines, one within green, and some broad but indistinct ones in the orange and red; and lastly, sodium, the single bright yellow line already mentioned.

It is impossible in our limited space to go more deeply into this subject, except to explain that in **absorption spectra**, which are produced by the passage of light through certain incandescent vapours and coloured liquids, the bright lines are not seen, but dark ones are formed instead. The dark lines of the solar spectrum are examples of such absorption bands, being doubtless caused by the passage of the light through the vapour surrounding the sun. By means of such absorption spectra the presence of the smallest quantities of bloodstains on clothes may be detected for medico-legal purposes and the genuine colouring matter of wines may be distinguished from pigments fraudulently introduced. Excellent special treatises have been written on this subject.

XVI. ANALYSIS BY CIRCULAR POLARIZATION.
THE SACCHARIMETER.

Crystals which do not belong to the regular system (notably calx spar), possess the power of *double* refraction. That is to say, when a ray of light falls upon them, it is divided into two rays, one of which follows the ordinary rule of refraction, while the other takes a totally different course. When these two rays are examined, they are found to differ in their behaviour: the one being capable of reflection by any suitable medium, while the other, when presented to the same medium, refuses to be reflected, but is entirely transmitted. Light when thus modified is said to be **polarized**, and the two rays are called respectively the "**ordinary**" and the "**extraordinary**" ray. Light may be also polarized by reflection from a piece of glass held at an angle of 56° 45', and indeed everything which interferes with the unrestricted course of a beam of light polarizes, to a greater or less extent. The most convenient polarizing medium is what is called a "**Nicol's prism.**" It is composed of a crystal of calx spar cut into two portions in the direction of its axis, and the two parts thus obtained cemented together with Canada balsam. When a beam of light enters the prism, it is polarized by the *first* portion of the crystal, and the **extraordinary** ray only passes through the **second** portion to the eye of the observer; while the **ordinary** ray is completely reflected away by the layer of Canada balsam, and so lost to view. If the extraordinary ray of polarized light thus obtained be examined by means of another Nicol's prism, it will be found that when the two prisms are placed with the principal sections parallel to each other, the ray will pass freely; but if the second prism be then turned round so that its chief section is at right angles to that of the first, the polarized ray will in turn be entirely reflected from the layer of balsam, and no light will now reach the observer's eye. This holds good, so long as nothing intervenes between the two prisms, but it has been found that certain bodies, such as sugar or quartz, possess the power, when interposed between the crossed prisms, of once more rendering the ray visible, and the observer finds that he has to turn the second prism still farther round to again produce total darkness. Such substances are said to possess the power of **circular polarization**, either in a "right-handed" or "left-handed" direction, according as it is necessary to turn the prism either to the right or left from its proper position to once more produce complete reflection of the polarized ray. Circular or rotary polarization was first observed by Arago; and the two remarkable phenomena by which it is characterized, are called **dextro- and lævo- gyration**; from whence are derived the adjectives **dextrogyrite** and **lævogyrite**. The direction of the rotation is indicated by the use of arrows, thus ↻ ↺. Cane-sugar, camphor, tartaric acid, cinchonine, castor oil, croton oil, and oil of lemons rotate the plane of the polarized ray to the right; while grape-sug

morphine, and oils of turpentine and valerian, cause a left-handed rotation. The amount of this rotation is fixed for each body, and increases with the quantity of the substance present in a given volume of solution, and also with the colour of the light employed, being least with red and increasing in regular order with yellow, green, blue, and violet, with which latter it is most marked. The chief application of circular polarization is to the analysis of sugar solutions, and the process is performed by means of the saccharimeter. This instrument in its simplest form consists of two Nicol's prisms; the one through which the light first passes being called the **polarizer**, and that to which the eye of the observer is applied being denominated the **analyzer**. The latter having been turned until darkness is obtained, the solution to be analysed is placed between them in a clear glass tube 10 inches in length and the analyzer is once more turned until darkness is obtained. The angle through which the prism has been turned is then read off from an approximate index and scale attached, and the amount of sugar calculated. An improved apparatus, invented by M. Soleil, is at present used, in which, instead of working from light to darkness, the colours produced by a pair of plates of quartz are utilized, a description of which will be found in any good work on Physics.

XVII. ELECTROLYSIS.

Electricity is one of the most powerful analytic forces with which the chemist has to deal. Its nature is less understood than that of the kindred forces of light and heat; but it is believed to be merely an aspect of the particles of matter towards one another, by virtue of which a dual force is made evident, manifesting itself in attractions and repulsions, and by producing chemical action accompanied frequently by effects of light and heat. It has two forms, the one termed **statical**, and characterized by great *density* or *tension*, so that it readily escapes by sparks; the other **dynamic**, or *current* electricity, which has a low tension but which can readily be obtained in enormous quantities. The former is that produced upon amber, resin, glass, sulphur, etc., by friction with such bodies as silk and flannel; and we have merely local sensations when it passes through the body. On the other hand a *galvanic* current direct from a battery passes through the body with such difficulty that we have no sensation. When a **coil** intervenes, we have the well-known "*electric shock*" since this augments the tension, or power of overcoming obstacles which resist its passage. A simple piece of electric apparatus formerly employed to produce a spark for the purpose of exploding gases was the **electrophorus**, which however is now superseded by the joint use of the battery and induction coil. It consisted of a sheet of resin upon a metal plate, and a brass disc furnished with a knob and a glass handle. The resin was excited by rubbing with flannel or a catskin, the disc placed on it, and the knob, when touched, gave a spark to any body connected with the earth.

Current electricity, of far greater importance, results from the action chemical agents upon various metals, the apparatus in its simplest form being called a **voltaic** or **galvanic cell** or **element**, and a combination of several cells being termed a **battery.**

A galvanic element has several forms; that of Grove, which is very extensively used and of great power, consists of an outer cell or jar of glass earthenware in which is placed a cylinder of zinc, an inner unglazed porous jar, and a sheet of platinum, both metals furnished with binding screws for attaching wires to them. The acids used are dilute sulphuric around the zinc, and strong nitric in contact with the platinum in the inner cell. The zinc constitutes the positive (or most attacked), the platinum

negative (or least attacked) metal; but when wires are attached to these and tipped with platinum, the end of the wire connected with the zinc is termed the **negative electrode**, whilst that in union with the platinum in the battery, is the **positive electrode**. To explain this apparent contradiction we must imagine that the current generated by the zinc passes through the fluid in the cell and then through the platinum, while at the same time an opposite current is generated from the platinum through the liquid to the zinc, and thus the effect of each current is felt at the ends of the wires from the opposite plate. These platinum electrodes (sometimes called poles), when placed near one another in a compound liquid, occasion the phenomena of **electrolysis**, which is simply the splitting up of conductors of electricity into their elements or into simpler forms. For instance, a solution of HCl gives off Cl at the positive electrode and the H at the negative, as a result of the axiom that unlike electricities attract and like repel one another, Cl itself being electro-negative and H electro-positive. Dealing with H_2SO_4 we get H_2 at one electrode and SO_4 at the other, the latter however at once splitting up into O (given off) and SO_3, which re-forms H_2SO_4 with the water present. This action is taken advantage of in the **voltameter**, an instrument for measuring the strength of an electric current by the amount of mixed gases (H and O) it will liberate from water. The instrument is a wide glass tube graduated in inches and fractions. It is filled with acidulated water and inverted over the two electrodes, when the two gases form and gradually displace the water from the tube. Sometimes separate tubes are used, one over the negative electrode, to collect the hydrogen, and the other over the positive, to collect the oxygen. The strength of the current is proportional to the quantity of gases set free within a given time. It is somewhat remarkable that all the bubbles of gas arise from the surfaces of the electrodes themselves and none from the intervening liquid. This is accounted for by supposing that when one of the gases, say H, is given off at one electrode, the O previously united with it seizes the H of an adjoining molecule of H_2O and thus sets free O to combine with the next H, until the last O reaches the second electrode and escapes. When sparks and strong heating effects (such as in the *electric light*, which is produced when two electrodes of carbon are approached so as nearly to touch each other) are desired, a number of cells must be used; but for the purpose of exploding gases the expense of these is saved by employing an *induction coil*. The principle of this instrument is, that when an interrupted current of low tension,—in fact a series of charges,—is made to pass into a coil of thick insulated copper wire, surrounded by a much longer coil of thin wire also carefully insulated, electricity of high tension, giving long and powerful sparks, is produced by induction.

XVIII. PYROLOGY.

Under this name are included all processes of analysis depending for their action on the use of fire, or, in other words, what were formerly called "*reactions in the dry way.*" The chief instruments used are the blow pipe and the Bunsen burner. The **blowpipe** is a tube with a narrow nozzle, by which a continuous current of air can be passed into an ordinary flame. The ordinary gas flame consists of three parts. (*a*) A non luminous nucleus in the centre. (*b*) A luminous cone surrounding this nucleus; and (*c*) An outer and only slightly luminous cone surrounding the whole flame. The centre portion (*a*) contains unaltered gas, which cannot burn for want of oxygen; that necessary element being cut off by the outer zones. In the middle portion (*b*) the gas comes in contact with a certain amount of oxygen, but not

enough to produce complete combustion; and therefore it is chiefly the hydrogen which burns here, the carbon separating and, by becoming intensely ignited, giving the light. In the outer zone (*c*) full combustion takes place, and the extreme of heat is arrived at, because chemical action is most intense. The outer flame, therefore, acts readily on oxidizable bodies because of the high temperature and the unlimited supply of air, while the luminous zone tends to take away oxygen by reason of the excess of unburned carbon or hydrocarbons therein existing. For these reasons the former is called the **oxidizing flame**, and the latter the **reducing flame**. The great analyst Fresenius thus describes the use of the blowpipe :—

The effect of blowing a fine stream of air across a flame is, first, to alter the shape of the flame, as, from tending upward, it is now driven sideways in the direction of the blast, being at the same time lengthened and narrowed; and, in the second place, to extend the sphere of combustion from the outer to the inner part. As the latter circumstance causes an extraordinary increase of the heat of the flame, and the former a concentration of that heat within narrower limits, it is easy to understand the exceedingly energetic action of the blowpipe flame. The way of holding the blowpipe and the nature of the blast will always depend upon the precise object in view, viz., whether the operator wants a *reducing* or an *oxidizing* flame. The easiest way of producing most efficient flames of both kinds is by means of coal-gas delivered from a tube terminating in a flat top with a somewhat slanting slit $\frac{4}{10}$ inch long and $\frac{8}{100}$ inch wide; as with the use of gas the operator is enabled to control and regulate not only the blowpipe flame, but the gas stream also. The task of keeping the blowpipe steadily in the proper position may be greatly facilitated by firmly resting that instrument upon some movable support.

The *reducing* flame is produced by keeping the jet of the blowpipe just on the border of a tolerably strong gas flame, and driving a moderate blast across it. The resulting mixture of the air with the gas is only imperfect, and there remains between the inner bluish part of the flame and the outer barely visible part a luminous and reducing zone, of which the hottest point lies somewhat beyond the apex of the inner cone. To produce the *oxidizing* flame, the gas is lowered, the jet of the blowpipe pushed a little further into the flame, and the strength of the current somewhat increased. This serves to effect an intimate mixture of the air and gas, and an inner pointed, bluish cone, slightly luminous towards the apex is formed, and surrounded by a thin, pointed, light-bluish, barely visible mantle. The hottest part of the flame is at the apex of the inner cone. Difficultly fusible bodies are exposed to this part to effect their fusion; but bodies to be oxidized are held a little beyond the apex, that there may be no want of air for their combustion.

The *current* is produced by the cheek muscles alone, and not with the lungs. The way of doing this may be easily acquired by practising for some time to breathe quietly with puffed-up cheeks and with the blowpipe between the lips; with practice and patience the student will soon be able to produce an even and uninterrupted current.

The *supports* on which substances are exposed to the blowpipe flame are generally either wood charcoal, or platinum wire or foil.

Charcoal supports are used principally in the reduction of metallic oxides, etc., or in trying the fusibility of bodies. The substances to be operated upon are put into small conical cavities scooped out with a penknife or with a little tin tube. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part upon the reduction of their oxides; in passing through the outer flame the metallic fumes are re-oxidized, and the oxide formed is deposited around the portion of matter upon the support. Such deposits are called incrustations. Many of these exhibit characteristic colours

leading to the detection of the metals. Thoroughly-burnt and smooth pieces of charcoal only should be selected for supports in blowpipe experiments, as imperfectly-burnt and knotty pieces are apt to spirt and throw off the matter placed on them.

The great use of charcoal lies (1) in its low degree of conductivity; (2) its porosity, which causes it to absorb fusible bodies and leave infusible ones upon its surface; and (3) its power of aiding the effects of the reducing flame.

Platinum wire and **foil** are used for supports in the oxidizing flame, and the former is specially employed for trying the action of fluxes and the colour communicable to the blowpipe or Bunsen flame. The platinum wire, when employed for making beads of borax or other fluxes, should be about 3 to 4 inches long with the end twisted into a small loop. The loop is then heated, and dipped while hot in the powdered borax, when it takes up a quantity which is then heated till it fuses to a clear bead formed within the loop. When cold, this is moistened and dipped in the powder to be tested, and again exposed to the flame, and the effect noted. For trying the colour impartable to the flame by certain metals, the wire is first cleaned by boiling in dilute nitric acid and then holding it in the flame until no colour is obtained. The loop is then dipped in the solution to be tested, and held near the flame till the adhering drop has evaporated to dryness, and then heated in the mantle of the flame near the apex of the inner cone, and the effect observed.

The **Bunsen burner** consists of a tube having at its base a series of holes to admit air, and also a small gas delivery tube. By means of this contrivance the gas is mixed with air before it burns, and more perfect oxidation, and consequently much greater heat, is secured. Looking attentively at the flame of a Bunsen burner, we distinguish in it an inner part and two mantles surrounding it. The inner part corresponds to the dark nucleus of the common gas flame, and contains the mixture of gas and air issuing from the burner. The mantle immediately surrounding the inner part contains still some unconsumed carbide of hydrogen, the outer mantle, which looks bluer and less luminous, consists of the last products of combustion. This hottest part,—lying in the mantles surrounding the inner part of the flame, in a zone extending a few hundredths of an inch upwards and downwards from the transverse section of the flame across the apex of the inner part,—has, according to Bunsen's calculation, a temperature of 4172° F. This is termed the *zone of fusion*. The outer margin of this zone of fusion acts as *oxidising flame*, the inner part of it as *reducing flame*. The spot where the reducing action is the most powerful and energetic lies immediately above the apex of the inner part of the flame. The Bunsen flame brings out the coloration which many substances impart to flames, and by which the qualitative analyst can detect many bodies, even though present in such minute quantities that all other means of analysis except the spectroscope fail to discover them. The subject of the coloration of flames will be discussed fully under each metal.

CHAPTER II.

DETECTION AND SEPARATION OF THE METALS.

FOR the purposes of qualitative analysis, we employ certain chemicals either in the solid or liquid state, which by producing given effects enable us to detect the existence of the substance searched for. These substances are always kept ready for use, and are called *reagents.* They are of three classes: 1st. **Group reagents**, which, by yielding a precipitate under certain conditions, prove the substance to be a member of a certain group of bodies. 2nd. **Separatory reagents**, by means of which the substance under examination is distinguished from the other members of the group. 3rd. **Confirmatory reagents**, by which the indications previously obtained are confirmed and rendered certain.

The Metals are divided into five groups, each of which has its group reagent, as follows:—

GROUP 1. Metals, the chlorides of which, being insoluble in water, are precipitated from their solution by the addition of **hydrochloric acid.** They are **silver, mercurous mercury,** and **lead** (the latter in cold strong solutions only).

GROUP 2. Metals, the sulphides of which, being insoluble in dilute hydrochloric acid, are precipitated from their solutions by the addition of **sulphuretted hydrogen** in the presence of hydrochloric acid. This group includes **mercury, lead, bismuth, copper, cadmium, antimony, tin, gold, platinum,** and the metalloid **arsenic,** and is divided into two sub-groups, as follows:—

A. Metals, the sulphides of which are insoluble in both dilute hydrochloric acid and ammonium sulphide. The precipitated sulphides separated by sulphuretted hydrogen, are therefore **insoluble** after washing **in ammonium sulphide.** They are **mercury, lead, bismuth, copper,** and **cadmium.**

B. Metals, the sulphides of which, although insoluble in dilute acids, are dissolved by alkalies, and the precipitates from their solutions by **sulphuretted hydrogen,** therefore dissolve in **ammonium sulphide.** They are **gold, platinum, tin, antimony,** and **arsenic.**

GROUP 3. Embraces those metals, the sulphides of which are soluble in dilute acids, but are insoluble in alkalies, and which consequently having escaped precipitation in Group 2, are now in turn precipitated by **ammonium sulphide.** They are **iron, nickel, cobalt, manganese,** and **zinc.** In this group are likewise included **aluminium** and **chromium,** which are precipitated as **hydrates** by the alkalinity of the **ammonium sulphide. Magnesium** would also be precipitated as hydrate, but as that would be inconvenient at this stage, its precipitation is prevented by the addition of **ammonium chloride,** in which its hydrate is soluble.

GROUP 4. Comprises metals, the chlorides and sulphides of which, being soluble, escape precipitation in the former groups, but the carbonates of which, being insoluble in water, are now precipitated by **ammonium carbonate.** They are **barium, strontium,** and **calcium. Magnesium** is not precipitated as carbonate owing to the presence of the **ammonium chloride,** already added with the sulphide in Group 3.

GROUP 5. Includes metals, the chlorides, sulphides, and carbonates of which, being soluble in **water** or in **ammonium chloride,** are not precipitated by any of the reagents already mentioned. They consist of **magnesium, lithium, potassium, sodium,** and **ammonium.**

As the analytical grouping of the metals is undoubtedly one which is most important to the student for practical purposes, we shall adhere to this arrangement in giving the methods for the detection and analytical separation of the metals used in Pharmacy.

GROUP I.

Metals precipitable as **chlorides** by the addition of hydrochloric acid to their solutions.

I. SILVER (Ag).

(a) *WET REACTIONS.*

(To be practised upon a solution of argentic nitrate—$AgNO_3$.)

1. **HCl** (*1st group reagent*) or any soluble chloride gives a curdy white precipitate of argentic chloride—AgCl—insoluble in boiling nitric acid but instantly soluble in ammonium hydrate. It is also soluble in KCy, $Na_2S_2O_3$, and in strong solutions of soluble chlorides.
2. **KHO** or **NaHO** both produce a brownish precipitate of argentic oxide, Ag_2O, insoluble in excess. A similar effect is produced by the hydrates of barium, strontium, and calcium.
3. $\mathbf{K_2CrO_4}$ gives a red precipitate of argentic chromate—Ag_2CrO_4 soluble in large excess of both nitric acid and ammonium hydrate, and therefore the solution should always be as neutral as possible.
4. $\mathbf{H_2S}$ and $\mathbf{NH_4HS}$, both produce black argentic sulphide—Ag_2S—insoluble in excess, but soluble in strong boiling nitric acid.
5. **KI** and **KBr** both produce curdy precipitates, the former yellow argentic iodide—AgI—insoluble in ammonium hydrate, and the latter argentic bromide—AgBr—dirty-white and slowly soluble in ammonium hydrate.
6. **KCy** gives a curdy-white precipitate of argentic cyanide—AgCy—readily soluble in excess, and also in boiling strong nitric acid
7. Many organic salts, such as formates and tartrates, boiled with solutions of silver, precipitate the metal as a mirror on the tube.
8. Fragments of copper, zinc, iron, and tin introduced into a solution of silver, all precipitate the metal.

(b) *DRY REACTION.*

(To be practised on argentic oxide—Ag_2O.)

Mixed with sodium carbonate and heated on charcoal before the blowpipe, a bead of silver is formed, hard, glistening, and soluble in nitric acid, yielding solution of argentic nitrate to which the wet tests may be applied.

(c) *SEPARATION.*

On adding hydrochloric acid, silver is precipitated as chloride together with the chlorides of mercurous mercury and lead, all other metals remaining

in solution. By washing the precipitate with boiling water, the plumbic chloride is dissolved out, and the residue is then treated with ammonium hydrate, which dissolves out the argentic chloride, and leaves mercurous oxide on the filter. The filtrate on dilution and acidulation with nitric acid, redeposits the argentic chloride in a pure condition.

II. MERCUROSUM $(Hg_2)''$.

(*a*) *WET REACTIONS.*

(To be practised on a solution of mercurous nitrate—$(Hg_2)''2NO_3$—prepared by acting upon a globule of mercury with cold and dilute nitric acid, so as not quite to entirely dissolve the metal.)

1. **HCl** (*1st group reagent*) gives a white precipitate of mercurous chloride, — $(Hg_2)''Cl_2'$ — turned to black mercuros-ammonium chloride — $NH_2(Hg_2)''Cl'$—by ammonium hydrate. It is also insoluble in boiling water, but soluble in strong nitric acid, being converted into a mixture of mercuric chloride—$HgCl_2$—and mercuric nitrate—$Hg2NO_3$.
2. **KHO** and **NaHO** both give black precipitates of mercurous oxide—Hg_2O—insoluble in excess.
3. $\mathbf{NH_4HO}$ produces a black precipitate of dimercuros-ammonium nitrate—$2NH_2(Hg_2)''NO_3H_2O$—also insoluble in excess.
4. $\mathbf{SnCl_2}$ boiled with the solution causes a grey precipitate of finely divided mercury, which if allowed to settle and then boiled with hydrochloric acid and some more stannous chloride, aggregates into a globule.

(*b*) *DRY REACTION.*

(To be tried upon mercurous iodide, *hydrargyri iodidum viride*, B.P.)

Mercurous compounds heated, break up into the corresponding mercuric salt, which sublimes, and metallic mercury, which also sublimes at a higher temperature.

(*c*) *SEPARATION.*

The addition of hydrochloric acid separates mercurous mercury from all other metals except silver and lead. The precipitated chlorides, having been washed free from lead by boiling water, are treated with ammonium hydrate, which dissolves the argentic chloride and leaves the mercury on the filter as black mercuros-ammonium chloride.

III. LEAD (Pb).

(*a*) *WET REACTIONS.*

(To be practised on a solution of plumbic acetate—$Pb2C_2H_3O_2$.)

1. **HCl** (*1st group reagent*) forms in cold strong solutions a white precipitate of plumbic chloride—$PbCl_2$—soluble in boiling water.
2. $\mathbf{H_2S}$ *after acidulation by* **HCl** (*2nd group reagent*) gives a black precipitate of plumbic sulphide—PbS—insoluble in ammonium sulphide. By treatment with boiling strong nitric acid it is decomposed, partly into plumbic nitrate, but chiefly into insoluble plumbic sulphate. It is entirely dissolved by hot dilute nitric acid with separation of sulphur.
3. $\mathbf{H_2SO_4}$ gives a white precipitate of plumbic sulphate—$PbSO_4$—slightly soluble in water, but rendered entirely insoluble by the addition of a little alcohol. It is decomposed by boiling strong hydrochloric acid,

and is also freely soluble in solutions of ammonium acetate or tartrate, containing an excess of ammonium hydrate.

4. **K_2CrO_4** gives a yellow precipitate of plumbic chromate—$PbCrO_4$—insoluble in acetic and very dilute nitric acids, but soluble in strong boiling nitric acid.
5. **KI** gives a yellow precipitate of plumbic iodide—PbI_2—soluble in boiling water, and crystallizing out on cooling in golden scales.
6. **KHO** and **NaHO** both cause white precipitates of plumbic hydrate—Pb2HO—soluble in excess, forming potassium or sodium plumbates—K_2PbO_2 and Na_2PbO_2.
7. **NH_4HO** causes a white precipitate of a white basic nitrate—$Pb(NO_3)HO$—soluble in excess.
8. **KCy** produces a white precipitate of plumbic cyanide—$PbCy_2$—insoluble in excess, but soluble in dilute nitric acid.
9. **Alkaline Carbonates** cause a precipitate of "white lead"—$(PbCO_3)_2Pb2HO$—insoluble in excess, and also in potassium cyanide.
10. Fragments of zinc or iron in the presence of a little acetic acid cause the separation of metallic lead in crystalline laminæ.

(*b*) *DRY REACTION.*

(To be practised on red lead—Pb_3O_4—or litharge—PbO.)

Heated on charcoal in the inner blow-pipe flame, a bead of metallic lead is formed, which is soft and malleable and soluble in dilute nitric acid. The solution thus obtained gives the wet tests for lead.

(*c*) *SEPARATION.*

On adding hydrochloric acid, a great part of the lead present will precipitate out as chloride, and may be separated from silver and mercurosum by washing the precipitate with boiling water, and testing in the solution with potassium chromate. The solution filtered from the hydrochloric acid precipitate is then treated with excess of sulphuretted hydrogen, which precipitates the remainder of the lead together with Hg, Bi, Cu, Cd, As, Sb, Sn, Au, and Pt. The precipitate is well washed free from chlorides, and is then digested in water containing ammonium sulphide, which dissolves everything except Hg, Pb, Bi, Cu, and Cd, left insoluble as sulphides. These mixed sulphides are then heated with strong nitric acid till red fumes cease, a few drops of sulphuric acid added, the whole washed in a test-tube with a little water, cooled, and mixed with an equal bulk of rectified spirit. Any precipitate will now consist only of mercuric sulphide and plumbic sulphate, the Bi, Cu, and Cd passing into solution. The precipitate is filtered out and percolated with ammonium acetate containing excess of ammonium hydrate, when the plumbic sulphate dissolves and is tested for in the liquid which passes through by adding potassium chromate.

GROUP II.

Metals which are not affected by acidulation with hydrochloric acid, but are precipitated by passing sulphuretted hydrogen through the acidulated solution.

Division A.

Metals which when precipitated by sulphuretted hydrogen as above, yield sulphides insoluble in ammonium sulphide.

I. MERCURICUM (Hg).

(a) WET REACTIONS.

(To be practised on a solution of mercuric chloride—$HgCl_2$.)

1. **H_2S** *after acidulation by* **HCl** (*2nd group reagent*) gives a black precipitate of mercuric sulphide—HgS—insoluble in ammonium sulphide and nitric acid, and only soluble in nitro-hydrochloric acid. Care must be taken that the sulphuretted hydrogen is passed really in excess, and that the whole is warmed gently, as unless this be done, the precipitate is not the true sulphide, but a yellowish-brown dimercuric sulpho-dichloride—Hg_2SCl_2. Although insoluble in any single acid, mercuric sulphide may be caused to dissolve in hydrochloric acid by the addition of a crystal of potassium chlorate.
2. **KHO** or **NaHO** both give a yellow precipitate of mercuric oxide—HgO—insoluble in excess.
3. **NH_4HO** produces a white precipitate of an insoluble mercur-ammonium chloride—$(NH_2Hg)Cl$—also insoluble in excess.
4. **KI** yields a red precipitate of mercuric iodide, soluble in excess of both the precipitant and of the mercuric salt.
5. **$SnCl_2$**, boiled with a mercuric solution, first precipitates mercurous chloride, and then forms metallic mercury, as in the case of mercurosum compounds.
6. **Alkaline Carbonates** (except ammonium carbonate) produce an immediate reddish-brown precipitate of mercuric oxy-carbonate.
7. Fragments of Cu, Zn, or Fe precipitate metallic mercury in the presence of dilute hydrochloric acid.

(b) DRY REACTION.

(To be tried on mercuric oxide—HgO—and on "Ethiops mineral"—HgS.)

All compounds of mercury are volatile by heat. The oxide breaking up into oxygen and mercury, which sublimes, while the sulphide sublimes unaltered, unless previously mixed with sodium carbonate or some reducing agent.

(c) SEPARATION.

By acidulating with hydrochloric acid, and passing sulphuretted hydrogen, *then washing the precipitate carefully with boiling water till free from chlorides*, and lastly digesting it in water containing some ammonium sulphide, we obtain mercuric sulphide associated only with the sulphides of Pb, Bi, Cu, and Cd. The precipitate is then treated with a little strong nitric acid, which dissolves all except the HgS. By washing into a test-tube, adding a few drops of sulphuric acid, and then an equal volume of rectified spirit, the HgS is deposited, mixed possibly with $PbSO_4$. If these be filtered out and percolated with ammonium acetate containing excess of ammonium hydrate, the $PbSO_4$ will be dissolved, and the HgS will be left on the filter as a *black* residue; which may then be dissolved in hydrochloric acid, by the aid of a crystal of potassium chlorate, and the mercury proved in the solution, by boiling with stannous chloride.

II. BISMUTH (Bi).

(a) WET REACTIONS.

(To be practised upon *bismuthi subnitras*, B.P., dissolved in water by the aid of the smallest possible quantity of nitric acid, and any excess of the latter carefully boiled off.)

1. **H_2S** *after acidulation by* **HCl** (*2nd group reagent*) gives a black precipitate of bismuth sulphide—Bi_2S_3—insoluble in ammonium sulphide, but soluble in boiling nitric acid.
2. **H_2SO_4** gives no precipitate (distinction from lead).
3. **NH_4HO, KHO,** and **NaHO** all give precipitates of white bismuthous hydrate—$Bi3HO$—insoluble in excess and becoming converted into the yellow oxide—Bi_2O_3—on boiling.
4. **H_2O** in excess to a solution from which the free acid has been as much as possible driven off by boiling, gives a white precipitate of a basic salt of bismuth. This reaction is more delicate in the presence of hydrochloric than of nitric acid; and the precipitate, which is in this case bismuth oxy-chloride—BiOCl—is insoluble in tartaric acid (distinction from antimonious oxy-chloride).
5. **K_2CrO_4** yields a yellow precipitate of bismuth oxy-chromate—$Bi_2O_2CrO_4$—soluble in dilute nitric acid, but not in potassium hydrate (distinction from plumbic chromate).
6. **KI** gives a brown bismuthous iodide, soluble in excess.
7. **Alkaline Carbonates** give white precipitates of bismuth oxy-carbonate, insoluble in excess.
8. Fragments of zinc added to a solution of bismuth cause a deposit of the metal as a dark grey powder.

(*b*) *DRY REACTION.*

(To be practised upon *bismuthi subnitras*, B.P.)

Mixed with sodium carbonate and heated on charcoal before the blowpipe, a hard bead of metallic bismuth is produced, and the surrounding charcoal is incrusted with a coating of oxide, deep orange-yellow while hot and becoming paler yellow on cooling.

(*c*) *SEPARATION.*

As already stated, bismuth is precipitated as sulphide by the action of sulphuretted hydrogen in the presence of hydrochloric acid. The precipitate having been washed and digested with ammonium sulphide is then heated in a small basin with strong nitric acid, and the whole having been washed into a test-tube with a little water, a few drops of sulphuric acid are added, and lastly, after cooling, some rectified spirit. This, as shown previously, separates the mercury and lead, leaving only Bi, Cu, and Cd in solution. The solution is then mixed with excess of ammonium hydrate, which precipitates the bismuth as white $Bi3HO$, and leaves the copper and cadmium in solution. By filtering out, dissolving in a little hydrochloric acid, and pouring into water, the production of a white precipitate entirely confirms the presence of bismuth.

III. COPPER (Cu).

(*a*) *WET REACTIONS.*

(To be practised with a solution of cupric sulphate—$CuSO_4$.)

1. **H_2S** *after acidulation with* **HCl** (*2nd group reagent*) forms a precipitate of brownish black cupric sulphide—CuS—which is nearly insoluble in ammonium sulphide but soluble in nitric acid. Its precipitation is prevented by the presence of potassium cyanide (distinction from cadmium). When long exposed to the air in a moist state, it oxidises to cupric sulphate and dissolves spontaneously.
2. **NH_4HO** causes a pale blue precipitate instantly soluble in excess, forming a deep blue solution of tetrammonio-cupric sulphate—$(NH_3)_4CuSO_4H_2O$.

3. **K_4FeCy_6** yields a chocolate-brown precipitate of cupric ferrocyanide—Cu_2FeCy_6. This test is very delicate and is not affected by the presence of a dilute acid, but does not take place in an alkaline liquid.
4. **KHO** or **NaHO** precipitate light-blue cupric hydrate—Cu2HO—insoluble in excess, but turning to black cupric oxy-hydrate—$(CuO)_2$Cu2HO—on boiling.
5. **$KNaC_4H_4O_6$** and **NaHO** added successively, the latter in excess, produce a deep-blue liquid (Fehling's solution), which when boiled with a solution of glucose (grape sugar) deposits brick-red cuprous oxide—Cu_2O.
6. The **Alkaline Carbonates** behave like their respective hydrates.
7. Fragments of zinc or iron precipitate metallic copper from solutions acidulated with HCl.

(*b*) *DRY REACTIONS.*

(To be practised upon cupric oxide—CuO—or *verdigris*—$Cu_2O2C_2H_3O_2$.)

1. Heated with Na_2CO_3 and KCy on charcoal, in the inner blowpipe flame, red scales of copper are formed.
2. Heated in the borax bead before the outer blowpipe flame, colours it green while hot, and blue on cooling. By carefully moistening the bead with $SnCl_2$ and again heating, this time in the inner flame, a red colour is produced.

(*c*) *SEPARATION.*

The addition of sulphuretted hydrogen in the presence of hydrochloric acid determines the precipitation of copper, together with the other sulphides of the 2nd group. Successive treatment with ammonium sulphide, nitric acid, sulphuric acid, and rectified spirit, as already shown (see *ante*), eliminates all but Bi, Cu, and Cd. The addition of excess of ammonium hydrate then separates bismuth and produces a deep-blue solution if copper be present.

IV. CADMIUM (Cd).

(*a*) *WET REACTIONS.*

(To be practised with a solution of cadmium iodide—CdI_2.)

1. **H_2S** *after acidulation with* **HCl** (*2nd group reagent*) gives a yellow precipitate of cadmium sulphide—CdS—insoluble in ammonium sulphide, but soluble in boiling nitric acid. This precipitate does not form readily in presence of much acid; but its production is not hindered by the addition of potassium cyanide (distinction from copper).
2. **NH_4HO** produces a white precipitate of cadmium hydrate—Cd2HO—soluble in excess.
3. **KHO** or **NaHO** both give precipitates of cadmium hydrate—Cd2HO—insoluble in excess (distinction from zinc).
4. **Alkaline Carbonates** precipitate cadmium carbonate—$CdCO_3$—insoluble in excess.

(*b*) *DRY REACTION.*

(To be practised on cadmium carbonate—$CdCO_3$.)

Heated on charcoal before the blowpipe, a brownish incrustation of oxide is produced, owing to the reduction to the metal and its subsequent volatilization and oxidation by the outer flame.

(*c*) *SEPARATION.*

Cadmium is precipitated, along with the other sulphides of the 2nd group, by the action of sulphuretted hydrogen in the presence of a slight trace of

hydrochloric acid. The precipitate having been subjected to the successive actions of ammonium sulphide, nitric acid, dilute sulphuric acid, and rectified spirit, and lastly of ammonium hydrate, all as already described (see *ante*), the resulting solution can only contain Cu and Cd. If the solution is colourless, no copper is present, and the addition of ammonium sulphide will produce the cadmium as a yellow sulphide; but if the solution be blue (indicating copper), then potassium cyanide is to be added till the colour is discharged and sulphuretted hydrogen passed, which will then precipitate the yellow cadmium sulphide, leaving the copper in solution.

GROUP II.

Division B.

Metals which are precipitated by sulphuretted hydrogen in the presence of hydrochloric acid, but yield sulphides which are soluble in ammonium sulphide.

I. ARSENIC (As).

(*a*) *WET REACTIONS.*

(To be practised with a solution of arsenious anhydride in boiling water slightly acidulated by hydrochloric acid.)

1. **H_2S**, *after acidulation with* **HCl**, causes a yellow precipitate of arsenious sulphide—As_2S_3—soluble in ammonium sulphide, forming ammonium sulpharsenite—$(NH_4)_3AsS_3$—but insoluble in strong boiling hydrochloric acid (distinction from the sulphides of Sb and Sn). This precipitate is also soluble in cold solution of official carbonate of ammonia (distinction from the sulphides of Sb, Sn, Au, and Pt). Dried and heated in a small tube with a mixture of Na_2CO_3 and KCy, it yields a mirror of arsenic.
2. Boiled with **KHO** *and a fragment of* **Zinc**, arseniuretted hydrogen—AsH_3—is evolved, which stains black a paper moistened with solution of argentic nitrate and held over the mouth of the tube during the ebullition (*Fleitmann's test*).
3. Boiled with ¼ of its bulk of **HCl** *and a slip of* **Copper**, a grey coating is deposited on the copper of cupric arsenide. On drying the copper carefully, cutting it into fragments, and heating in a wide tube, a crystalline sublimate of arsenious anhydride—As_2O_3—is obtained, which, when dissolved in water, gives a yellow precipitate of argentic arsenite —Ag_3AsO_3—with solution of ammonio-nitrate of silver (*Reinch's test*).
4. Placed in a gas bottle furnished with a jet, together with dilute sulphuric or hydrochloric acid and a few fragments of zinc, arseniuretted hydrogen—AsH_3—is evolved, which may be lighted at the jet and burns with a lambent flame, producing As_2O_3. If a piece of cold porcelain be held in the flame, dark spots of arsenic are obtained, readily volatile by heat and soluble in solution of chlorinated lime (*Marsh's Test*).

Note.—For reactions of **arsenites** and **arseniates**, see Acidulous Radicals.

(*b*) *DRY REACTION.*

(To be practised on arsenious anhydride—As_2O_3.)

Heated in a small tube with Na_2CO_3 and KCy, a mirror of arsenic is produced, accompanied by a garlic-like odour.
with black flux.

(c) SEPARATION.

By passing sulphuretted hydrogen in the presence of hydrochloric acid, arsenious sulphide is precipitated, together with the other sulphides of the second group. The precipitate is washed and digested with water containing ammonium sulphide, which dissolves the sulphides of As, Sb, Sn, Au, and Pt. The solution is filtered, and a slight excess of HCl having been added, these sulphides are reprecipitated. The precipitate is filtered out and shaken up with a cold solution of official carbonate of ammonia, which dissolves only the arsenious sulphide, leaving the sulphides of Sb, Sn, Au, and Pt insoluble. From this solution, after filtration, the arsenious sulphide may be reprecipitated by hydrochloric acid, dried, and confirmed by heating with Na_2CO_3 and KCy, and getting a mirror of arsenic on the tube.

II. ANTIMONY (Sb).

(a) WET REACTIONS.

(To be practised with a solution of antimonium tartaratum, B.P.)

1. **H_2S**, *after acidulation by* **HCl** causes an orange precipitate of antimonious sulphide—Sb_2S_3—soluble in ammonium sulphide, forming ammonium sulphantimonite—$(NH_4)_3SbS_3$—also soluble in strong boiling hydrochloric acid, forming antimonious chloride—$SbCl_3$—but insoluble in cold solution of official carbonate of ammonia.
2. **KHO** *and* **NaHO** produce precipitates of antimonious oxide readily soluble in excess to form antimonites (K_3SbO_3 or Na_3SbO_3).
3. Acidulated with **HCl** and introduced into a **platinum dish** with a rod of **zinc** so held that it touches the platinum *outside* the liquid, a black stain of metallic antimony is produced closely adherent to the platinum. This stain is not dissolved by HCl (tin reduced in the same manner is granular and soluble in boiling HCl).
4. **Reinch's test** (see arsenic) produces a black coating on the copper, which, when heated, forms an amorphous sublimate of Sb_2O_3 *close to the copper*, and insoluble in water, but dissolved by a solution of cream of tartar in which H_2S then produces the characteristic orange sulphide.
5. **Marsh's test** (see arsenic) yields stains of antimony on the porcelain not nearly so readily volatile by heat as in the case of arsenic, and not discharged by solution of chlorinated lime.
6. **Fleitmann's test** will not act with antimony at all (distinction from arsenic).

(b) DRY REACTION.

(To be practised on antimonious oxide—Sb_2O_3).

Heated on charcoal with Na_2CO_3 and KCy before the blowpipe, a bead of metallic antimony is formed and copious white fumes of the oxide are produced.

(c) SEPARATION.

Antimony is obtained as sulphide, associated only with As, Sn, Au, and Pt by precipitating with sulphuretted hydrogen in the presence of hydrochloric acid, and digesting the precipitate in water containing ammonium sulphide. The solution thus obtained yields the sulphides on acidulation with hydrochloric acid, and by shaking them up with solution of official carbonate of ammonia, the arsenic is dissolved (see *ante*). The precipitate, which can only now contain the sulphides of Sb, Sn, Au, and Pt, is boiled with strong hydrochloric acid, which dissolves the Sb and Sn and leaves the Au and Pt insoluble. The solution is then slightly diluted and introduced into a platinum

dish, and a rod of zinc held in the fluid so that it touches the platinum outside the liquid, when both the metals are deposited,—the Sb as a black stain closely adhering to the platinum, and the Sn in the form of granules. Boiling with strong hydrochloric acid will then dissolve the tin, and leave the antimony.

III. TIN (Sn^{ii} or Sn^{iv}).

(a) *WET REACTIONS.*

(To be practised with a solution of stannous chloride—$SnCl_2$—and one of stannic chloride—$SnCl_4$—prepared by warming the stannous solution with a little nitric acid.)

1. **H_2S**, *after acidulation with* **HCl**, produces a brown or yellow precipitate of SnS or SnS_2 respectively, both soluble in ammonium sulphide and in boiling hydrochloric acid.
2. **KHO** or **NaHO** both produce white precipitates of Sn2HO or Sn4HO soluble in excess, the former to produce *stannites* and the latter *stannates*. The stannous solution is, however, reprecipitable on boiling, while the stannic is not.
3. **NH_4HO** produces similar precipitates, very difficultly soluble in excess.
4. Acidulated by **HCl**, and introduced into a platinum dish with a rod of **zinc** so held in the fluid that it touches the platinum *outside* the liquid, granules of metallic tin are deposited, soluble in boiling HCl, to form stannous chloride.
5. **$HgCl_2$** boiled with *stannous* salts, deposits a grey precipitate of metallic mercury.

(b) *DRY REACTION.*

(To be practised on *putty powder*—SnO_2.)

Heated on charcoal with Na_2CO_3 before the blowpipe, a bead of metallic tin is produced, and a white incrustation of oxide is formed on the charcoal.

(c) *SEPARATION.*

The separation of tin has already been described in connection with that of antimony; and it is only necessary, after dissolving the granules in strong hydrochloric acid, to prove the presence of Sn by boiling with mercuric chloride.

IV. GOLD (Au).

(a) *WET REACTIONS.*

(To be practised with a solution of auric chloride—$AuCl_3$.)

1. **H_2S** (*group reagent*) in the presence of HCl gives black auric sulphide —Au_2S_3. If the solution be hot, aurous sulphide—Au_2S—falls. Both are only soluble in nitro-hydrochloric acid, but they are soluble in ammonium sulphide when it is yellow.
2. **NH_4HO** precipitates reddish ammonium aurate, or *fulminating gold*—$Au_2(NH_3)_2O_2$—but KHO gives no result.
3. **$H_2C_2O_4$** (or **$FeSO_4$**) when boiled with an acid solution throws down Au. Reducing agents generally act thus. The liquid containing the metal may exhibit a blue, green, purple, or brown colour.
4. **$SnCl_2$** throws down a brownish or purplish precipitate, known as "pu of Cassius," consisting of the mixed oxides of gold an
5. **Zn, Cu, Fe, Pt**, or almost any metal, give a precipit finely divided state.

(*b*) *DRY REACTION.*

(To be practised on any gold salt.)

Heated on charcoal with Na_2CO_3, the metal is produced.

(*c*) *SEPARATION.*

Gold is separated from other metals with great readiness, by taking advantage of the instability of its salts. To an acid solution oxalic acid or ferrous sulphate is added in excess, the mixture warmed and allowed to stand twenty-four hours, when all the gold present is found in the metallic state and may be filtered out.

V. PLATINUM (Pt).

(*a*) *WET REACTIONS.*

(To be tested with a solution of platinic chloride—$PtCl_4$.)

1. **H_2S** (*2nd group reagent*) in presence of HCl, gives a *brown* precipitate of platinic sulphide—PtS_2. This precipitate forms slowly, and is readily dissolved by yellow ammonium sulphide.
2. **KCl** *in presence of* **HCl**, especially after addition of alcohol, produces a yellow crystalline precipitate of potassium platinic chloride—PtK_2Cl_6—soluble to a moderate extent in water, but not in alcohol. Decomposition takes place when this is strongly heated, metallic Pt and KCl remaining.
3. **NH_4Cl** gives a precipitate of ammonium platinic chloride—$Pt(NH_4)_2Cl_6$ which is almost identical in properties, but is more readily decomposed by heat, pure platinum remaining.
4. **Zn**, **Fe**, and several other metals decompose platinic salts with the production of the metal.

(*b*) *DRY REACTION.*

(To be practised upon potassium platinic chloride—PtK_2Cl_6.)

Heat on charcoal, with or without Na_2CO_3, before the blow-pipe. The metal is produced by reduction.

(*c*) *SEPARATION.*

Platinum is readily separated by taking advantage of the fact that its compounds with potassium or ammonium and chlorine are insoluble in alcohol. To a clear solution containing the Pt as chloride, add NH_4Cl, evaporate over a water bath till the mixture be dry, add a little water and evaporate again, then pour over some methylated spirit and a drop or two of HCl. On filtering, all other metals are dissolved out as chlorides, leaving the Pt salt alone on the filter.

GROUP III.

Metals which escape precipitation by sulphuretted hydrogen in presence of hydrochloric acid, but which are precipitated by ammonium sulphide in the presence of ammonium hydrate, ammonium chloride having been previously added to prevent the precipitation of magnesium.

Division A.

Metals which, *in the ensured absence of organic matter*, are precipitated as hydrates by the addition of the ammonium chloride and ammonium hydrate only.

I. IRON (*Ferrous*, **Fe**; and *ferric*, **Fe_2**).

(*a*) *WET REACTIONS.*

(To be practised successively on solutions of ferrous sulphate—$FeSO_4$—and ferric chloride—Fe_2Cl_6.)

1. **NH_4HO** *in the presence of* **NH_4Cl** (*group reagent*) yields either a dirty-green precipitate of ferrous hydrate—$Fe2HO$—or a reddish-brown precipitate of ferric hydrate—Fe_26HO. The former is *slightly* soluble in excess, but the latter is insoluble, and it is therefore preferable always to warm the solution with a little nitric acid, to ensure the raising of the iron to the ferric state, before adding the ammonium hydrate. The presence of organic acids, such as tartaric or citric, prevents the occurrence of this reaction; and therefore, if any such admixture be suspected, the solution should first be evaporated to dryness, the residue heated to redness, and then dissolved in a little hydrochloric acid, heated with a drop or two of nitric acid, diluted, and lastly, the NH_4Cl and NH_4HO added and boiled.
2. **NH_4HS**, added to a neutral or alkaline solution, produces a precipitate of ferrous sulphide—FeS—which is black (distinction from Al, Ce, Cr, Mn, and Zn), and readily soluble in cold diluted hydrochloric acid (distinction from the black sulphides of Ni and Co). This reaction takes place even in the presence of organic matter, and the precipitated sulphide, if exposed to the air, gradually oxidizes to ferrous sulphate—$FeSO_4$—and disappears. It is insoluble in acetic acid (distinction from MnS).
3. **K_4FeCy_6**, in a neutral or slightly acid solution, gives, with ferrous salts, a white precipitate (rapidly changing to pale blue) of Everett's salt—potassium ferrous ferrocyanide—$K_2FeFeCy_6$—and with ferric salts, a dark blue precipitate of Prussian blue—ferric ferrocyanide $(Fe_2)_2 3FeCy_6$. These precipitates are decomposed by alkalies, producing the hydrates of iron, and forming a ferrocyanide of the alkali in solution; but the addition of hydrochloric acid causes the re-formation of the original precipitate.
4. **$K_6Fe_2Cy_{12}$** gives, with ferrous salts, in neutral or slightly acid solutions, a dark blue precipitate of Turnbull's blue—ferrous ferricyanide, $Fe_3Fe_2Cy_{12}$—but with ferric salts it gives no precipitate, simply producing a brownish liquid. With alkalies, Turnbull's blue is decomposed, yielding black ferroso-ferric hydrate, and a ferricyanide of the alkali; but the addition of hydrochloric acid reproduces the original blue.
5. **KCyS** gives no precipitate with ferrous salts, but with ferric compounds it yields a deep blood-red solution. This colour is not discharged by dilute hydrochloric acid (distinction from ferric acetate), but immediately bleached by solution of mercuric chloride (distinction from ferric meconate).
6. **KHO**, or **NaHO**, produces effects similar to those of ammonium hydrate.
7. **Na_2HPO_4** *in the presence of* **$NaC_2H_3O_2$** *or* **$NH_4C_2H_3O_2$** gives a whitish gelatinous precipitate of ferrous or ferric phosphates—Fe_32PO_4 or Fe_22PO_4—insoluble in acetic acid, but soluble in hydrochloric acid. The previous addition of citric or tartaric acids prevents this reaction.
8. **$NaC_2H_3O_2$**, added in excess to *ferric* salts, produces a deep red solution of ferric acetate—$Fe_26C_2H_3O_2$—which on boiling deposits as a reddish brown ferric oxyacetate—$Fe_2O4C_2H_3O_2$. This precipitate dissolves slightly on cooling; but iron can be entirely precipitated in this form if the solution be instantly filtered while hot.

9. **Alkaline Carbonates**, added to a ferrous salt, precipitate white ferrous carbonate—$FeCO_3$—but with ferric salts throw down the reddish-brown ferric hydrate already described.

(*b*) *DRY REACTIONS.*

(To be practised on *ferri peroxidum hydratum*, B.P.)

1. Heated on charcoal before the inner blowpipe flame, a black magnetic powder is obtained, which is not the metal, but is ferroso-ferric oxide—Fe_3O_4.
2. Heated in the borax bead in the inner blowpipe flame, a bottle-green colour is produced; but in the outer flame the bead is deep red while hot, and very pale yellow when cold.

(*c*) *SEPARATION.*

The solution, after treatment with sulphuretted hydrogen, in the presence of hydrochloric acid, so as to cause the entire separation of the metals of the first and second groups, is evaporated to dryness, and heated to ensure the decomposition of any organic matter. The residue is drenched with strong hydrochloric acid, and then water added, and the whole boiled, adding a few drops of HNO_3 to raise all the iron to the ferric state. On adding NH_4Cl to this solution, and then NH_4HO in slight but distinct excess, boiling and filtering rapidly, the iron is precipitated as ferric hydrate, and with it may also be found the hydrates of Ce, Cr, and Al. The precipitate is fused with excess of $KNaCO_3$ and KNO_3, and the residue boiled with water, when everything dissolves but Fe and Ce, which remain as red oxides. This residue may then be dissolved in HCl, and the iron tested for by K_4FeCy_6 in a portion of the solution.

[For separation of iron in the presence of phosphoric acid, see *Separation of Phosphates*, Chap. III.]

II. CERIUM (Ce).

(*a*) *WET REACTIONS.*

(To be practised on Cerous Chloride—$CeCl_2$—prepared by boiling *cerii oxalas*, B.P., with sodium hydrate, washing the insoluble cerous hydrate with boiling water, and dissolving it in the least possible excess of hydrochloric acid.)

1. **NH_4HO**, *in the presence of* **NH_4Cl** (*group reagent*) gives a white precipitate of cerous hydrate—Ce2HO—insoluble in excess.
2. **KHO** and **NaHO** give a similar precipitate, turning to yellow ceroso-ceric oxide—Ce_3O_4—on the addition of chlorine water.
3. **$(NH_4)_2C_2O_4$** gives a white precipitate of cerous oxalate—CeC_2O_4—insoluble in excess, and not readily dissolved even by hydrochloric acid. The presence of citric or tartaric acid does not interfere with this reaction.
4. **K_2SO_4** in a saturated solution causes the formation of white crystalline potassium cerium sulphate—$K_2Ce(SO_4)_2$—soluble in hot water.

(*b*) *DRY REACTIONS.*

(To be practised on *cerii oxalas*, B.P.)

1. Heated to redness in contact with the air, a deep red residue of ceric oxide—Ce_2O_3—is obtained, difficultly soluble even in strong hydrochloric acid.
2. Heated in the borax bead, cerium behaves like iron in the outer flame, but the inner flame yields a colourless or opaque yellow bead.

(*c*) *SEPARATION.*

Proceed exactly as for iron, and to the remainder of the solution, after testing the portion for that metal, add citric acid, and then excess of ammonium hydrate. The presence of the organic acid prevents the precipitation of the iron by the ammonium hydrate, and then the addition of ammonium oxalate proves the cerium. This separation is equally good in the presence of phosphoric acid.

III. ALUMINIUM (Al).

(*a*) *WET REACTIONS.*

(To be practised on a solution of *alum*, B.P.—$NH_4Al(SO_4)_2 12H_2O$.)

1. **NH_4HO** *in presence of* **NH_4Cl** (*group reagent*) gives a gelatinous white precipitate of aluminic hydrate—$Al_2 6HO$. This precipitate is slightly soluble in a large excess of the precipitant, but separates completely on boiling.
2. **KHO** and **NaHO** both give a similar precipitate, soluble in excess, but reprecipitated by boiling with an excess of ammonium chloride, or by neutralizing with hydrochloric acid, and boiling with a slight excess of ammonium hydrate.
3. **Na_2HPO_4** *in the presence of* $NaC_2H_3O_2$ or $NH_4C_2H_3O_2$ gives a white precipitate of aluminic phosphate—$AlPO_3$—insoluble in hot acetic acid, but soluble in hydrochloric acid. The presence of citric or tartaric acids prevents the occurrence of this reaction.

(*b*) *DRY REACTION.*

(To be practised on dried *alum*, B.P.)

Heat strongly on charcoal before the blowpipe, when a strong incandescence is observed, and a white residue is left. Moisten this residue with a drop of solution of cobaltous nitrate—$Co2NO_3$—and again heat strongly, when a blue mass is left. This test is not decisively characteristic, as other substances, such as zinc and earthy phosphates, show somewhat similar colours.

(*c*) *SEPARATION.*

Aluminium is precipitated by ammonium hydrate in the presence of ammonium chloride, together with Fe, Ce, and Cr, as already described in the separation of iron. The precipitate is fused with $KNaCO_3$ and KNO_3, and the residue digested with water and filtered. This yields a solution containing the aluminium hydrate dissolved in excess of the alkali, and the chromium as a soluble chromate. By acidulating with acetic acid, and adding disodium hydrogen phosphate and boiling, the Al is precipitated as phosphate, and the chromate is not affected.

IV. CHROMIUM (Cr).

(*a*) *WET REACTIONS.*

(To be practised on a solution of potassium chromic chloride prepared by dissolving potassium dichromate—$K_2Cr_2O_7$—in water, acidulating with hydrochloric acid, heating and dropping in rectified spirit till the solution turns green.)

1. **NH_4HO** *in the presence of* **NH_4Cl** (*group reagent*) precipitates green chromic hydrate—$Cr_2 6HO$—slightly soluble in excess, but entirely reprecipi-

tated on boiling. The presence of citric or tartaric acid interferes with the completeness of this reaction.

2. **KHO**, or **NaHO**, gives similar precipitates; freely soluble in excess when cold, but entirely reprecipitable by continued boiling.
3. **NaOCl**, or **PbO_2**, boiled with an alkaline solution of a chromium salt, produces a yellow solution of sodium chromate—Na_2CrO_4.
4. **Na_2HPO_4**, *in the presence of* **$NaC_2H_3O_2$** or **$NH_4C_2H_3O_2$** throws down pale green chromic phosphate—$CrPO_4$—soluble when freshly precipitated in excess of hot acetic acid, and freely soluble in hydrochloric acid. The presence oforganic acids prevents this reaction.

(*b*) *DRY REACTIONS.*

1. Heated in the borax bead in the inner blowpipe flame, a fine green colour is obtained.
2. Fused on platinum foil, with a mixture of $KNaCO_3$ and KNO_3, a yellow residue is obtained, consisting of chromates of the alkaliesused. This mass is soluble in water, yielding a yellow solution turned deeper in colour by the addition of hydrochloric acid, owing to the formation of dichromates, and becoming green on warming and dropping in rectified spirit.

(*c*) *SEPARATION.*

Chromium is precipitated as hydrate by NH_4Cl and NH_4HO, after separating the metals of the first two groups. [See Separation of Fe.] The precipitate is fused with $KNaCO_3$ and KNO_3, which forms potassium chromate, known by the bright yellow colour of the residue. On boiling with water, acidulating with acetic acid, and adding disodium hydrogen phosphate, and again boiling, any aluminium is precipitated as phosphate, and the chromate remains as a yellow solution turned green by boiling with HCl and rectified spirit. This course is only good in the ensured absence of phosphoric acid (for details in presence of which see *Separation of Phosphates*, Chap. III.).

GROUP III.

Division B.

Metals the hydrates of which, being soluble in excess of ammonium hydrate in the presence of ammonium chloride, escape precipitation by that reagent, but are separated as insoluble sulphides by the addition of ammonium sulphide to the same liquid.

I. MANGANESE (Mn).

(*a*) *WET REACTIONS.*

(To be practised on a solution of potassium manganous chloride, prepared by heating a solution of potassium permanganate with hydrochloric acid, and dropping in rectified spirit until a colourless solution is obtained.)

1. **NH_4HS** *in the presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) precipitates a flesh-coloured manganous sulphide—MnS—soluble in dilute and cold hydrochloric acid (distinction from the sulphides of Ni and Co). It is also soluble in acetic acid (distinction from zinc sulphide). This precipitate forms sometimes very slowly and only after gently warming. If a good excess of NH_4Cl has not been added, or if, after adding the excess of ammonium hydrate, the solution be exposed to the air, a portion of the manganese will sometimes precipitate sponta-

neously, as manganic dioxyhydrate—$Mn_2O_2 2HO$—and be found with the iron, etc., in the first division of the third group. In this case its presence will be easily made manifest during the fusion for chromium by the residue being green. It is therefore evident that small quantities of manganese cannot be perfectly separated from large quantities of iron by NH_4Cl and NH_4HO only.

2. **KHO** and **NaHO** both yield precipitates of manganous hydrate insoluble in excess, and converted by boiling into dark brown manganic dioxyhydrate—$Mn_2O_2 2HO$.
3. **NH_4HO** gives a similar precipitate, soluble in excess of ammonium chloride, but gradually depositing as $Mn_2O_2 2HO$ by exposure to the air. For this reason, if the presence of manganese be suspected, the addition of NH_4Cl and NH_4HO must be followed by instant filtration, and any cloudiness coming in the filtrate must be simply taken as indicating manganese, and disregarded.
4. **K_4FeCy_6** gives a precipitate of manganous ferrocyanide—Mn_2FeCy_6—very liable to be mistaken for the corresponding zinc compound.

(*b*) *DRY REACTIONS.*

(To be practised on manganese peroxide—$Mn O_2$.)

1. Fused on platinum foil with $KNaCO_3$ and KNO_3, a green mass of manganates of the alkalies is formed. This residue is soluble in water, yielding a green solution, turning purple on boiling, owing to the formation of permanganates. The solution is rendered colourless by heating with hydrochloric acid and dropping in rectified spirit, the operation being accompanied by the odour of aldehyd.
2. Heated in the borax bead in the outer blowpipe flame, a colour is produced which is violet-red while hot, and amethyst on cooling. The bead is rendered colourless by the reducing flame.

(*c*) *SEPARATION.*

Manganese, when precipitated as sulphide by ammonium sulphide in the presence of ammonium hydrate, is easily separated by dissolving in dilute hydrochloric acid, which does not affect the sulphides of Ni and Co. The solution is then boiled with *excess* of sodium hydrate, which precipitates the manganese and leaves the zinc. The precipitate is then confirmed by fusion with $KNaCO_3$ and KNO_3, when it gives the characteristic green mass. Another way is to add to the hydrochloric acid solution an excess of sodium acetate, and then pass sulphuretted hydrogen, which will precipitate the other metals, leaving the manganese in solution because its sulphide alone of all the group is soluble in acetic acid.

II. ZINC (Zn).

(*a*) *WET REACTIONS.*

(To be practised on solution of zinc sulphate—$ZnSO_4$.)

1. **NH_4HS** *in the presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) gives a white precipitate of zinc sulphide—ZnS—insoluble in acetic acid, but readily soluble in dilute hydrochloric acid.
2. **KHO**, **NaHO**, and **NH_4HO** all give precipitates of gelatinous white zinc hydrate, soluble in excess to form zincates. The addition of sulphuretted hydrogen or ammonium sulphide reprecipitates the zinc as zinc sulphide—ZnS.

3. **K_4FeCy_6** gives a gelatinous white precipitate of zinc ferrocyanide—Zn_2FeCy_6—insoluble in dilute acids.
4. **Alkaline Carbonates** precipitate official *zinci carbonas*—zinc hydrato-carbonate—$ZnCO_3(Zn2HO)_2H_2O$—insoluble in excess of the carbonates of potassium and sodium, but soluble in that of ammonium. The latter solution, diluted and boiled, deposits the oxide.

(*b*) *DRY REACTIONS.*

(To be practised on *zinci carbonas*, B.P.)

1. Salts of zinc heated leave the oxide, yellow while hot, and white on cooling.
2. Heated on charcoal before the blowpipe an incrustation forms, yellow while hot, and white on cooling. Moisten with a drop of cobaltous nitrate—$Co2NO_3$—and again heat in the outer flame, when a fine green colour is produced.

(*c*) *SEPARATION.*

The addition of ammonium sulphide in the presence of ammonium chloride and ammonium hydrate precipitates zinc sulphide together with the other metals of the group. This precipitate is treated with cold dilute hydrochloric acid, which dissolves the Zn and Mn, and leaves Ni and Co insoluble. The solution boiled with excess of sodium hydrate deposits the Mn; and the filtrate treated with excess of acetic acid and sulphuretted hydrogen deposits the Zn as sulphide.

III. NICKEL (Ni).

(*a*) *WET REACTIONS.*

(To be practised on a solution of nickelous sulphate—$NiSO_4$.)

1. **NH_4HS** *in the presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) gives a black precipitate of nickelous sulphide—NiS—slightly soluble in excess but entirely precipitated on boiling. It is not soluble in cold dilute hydrochloric or in acetic acid, but requires boiling with strong hydrochloric acid and sometimes even the addition of a drop or two of nitric acid.
2. **KHO** or **NaHO** both give a green precipitate of nickelous hydrate—Ni2HO—unaltered by boiling (distinction from cobalt).
3. **KNO_2** added to a neutral solution, followed by an excess of acetic acid, gives no precipitate (after standing some hours) on the addition of potassium acetate and rectified spirit (very useful separation from cobalt).
4. **KCy** in excess produces a greenish-yellow precipitate of nickelous cyanide—$NiCy_2$—which quickly redissolves. On adding a drop of hydrochloric acid and boiling in a fume chamber, and repeating this till no more fumes of hydrocyanic acid come off, and then adding sodium hydrate, a precipitate of nickel hydrate is produced. It is better, although less convenient, to use a strong solution of chlorinated soda—NaClNaClO—in the last stage, when nickelic hydrate—Ni6HO—is slowly precipitated (distinction from Co, which gives no precipitate).
5. **Alkaline Carbonates** behave, so far as colour and solubility in excess is concerned, like their respective hydrates.

(*b*) *DRY REACTIONS.*

1. Heated on charcoal with Na_2CO_3 in the inner blowpipe flame, a grey metallic and magnetic powder is produced.

Heated in the borax bead in the outer blowpipe flame, red to violet brown

is produced while hot, and a yellowish to sherry red when cold. These colours might be mistaken for those of iron; but on fusing a small fragment of potassium nitrate with the bead, its colour at once changes to blue or dark purple (distinction from Fe).

IV. COBALT (Co).

(*a*) *WET REACTIONS.*

(To be practised on a solution of cobaltous nitrate—$Co2NO_3$.)

1. **NH_4HS** *in the presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) gives a black precipitate of cobaltous sulphide—CoS—insoluble in acetic and cold dilute hydrochloric acid, and requiring to be boiled with the strongest HCl, often with the addition of a drop or two of nitric acid before solution is effected.
2. **KHO**, or **NaHO**, gives a blue precipitate of cobaltous hydrate—Co2HO—rapidly changing to pink on boiling (distinction from nickel).
3. **KCy** gives a light brown precipitate of cobaltous cyanide, rapidly soluble in excess but reprecipitated by excess of dilute hydrochloric acid. If, however, the HCl be added drop by drop just so long as it causes the evolution of hydrocyanic acid fumes on boiling,* soluble potassium cobalticyanide—$K_6Co_2Cy_{12}$—results, which is not decomposed by hydrochloric acid; nor is any precipitate produced on adding excess of sodium hydrate or chlorinated soda (distinction from nickel).
4. **Alkaline Carbonates** throw down basic carbonates, behaving like the respective hydrates.

(*b*) *DRY REACTIONS.*

1. Heated on charcoal with Na_2CO_3 in the inner blowpipe flame, the cobalt separates as a grey magnetic powder.
2. Heated in the borax bead, first in the *outer* and then in the *inner* flame, a fine blue colour is produced. It is an important distinction of cobalt from copper, manganese, etc., that *prolonged heating in the inner flame does not affect this blue.*

(*c*) *SEPARATION.*

The sulphides of nickel and cobalt are easily separated from all the other of this group by their insolubility in cold dilute hydrochloric acid. They may then be dissolved in strong acid, the solution diluted a little and *nearly* neutralized by KHO, and then the cyanide separation above described applied. It is to be noted however, that no truly satisfactory separation of Ni from Co exists.

GROUP IV.

Metals, the hydrates and sulphides of which, being soluble, are not precipitated by the addition of NH_4HO and NH_4HS in the presence of NH_4Cl, but separate as insoluble carbonates on the addition of ammonium carbonate to the same solution.

I. BARIUM (Ba).

(*a*) *WET REACTIONS.*

(To be practised on a solution of barium chloride—$BaCl_2$.)

1. **$(NH_4)_2CO_3$** *in the presence of* NH_4Cl *and* N

* This must be done in a fume chamber,
should happen to escape into the room.

duces a white precipitate of barium carbonate, $BaCO_3$, soluble with effervescence in dilute acetic acid.

2. **H_2SO_4** and all **soluble Sulphates** give a white precipitate of barium sulphate—$BaSO_4$—insoluble in ammonium acetate or tartrate (distinction from $PbSO_4$) and also in boiling nitric acid.
3. **K_2CrO_4** gives a yellow precipitate of barium chromate—$BaCrO_4$—insoluble in water and in dilute acetic acid, but soluble in hydrochloric acid (distinction from Sr and Ca).
4. **$NH_4C_2O_4$** gives a white precipitate of barium oxalate—BaC_2O_4—not readily formed in the presence of much acetic acid.
5. **Na_2HPO_4** gives a white precipitate of barium hydrogen phosphate—$BaHPO_4$—soluble in acetic acid, and to some extent in ammonium chloride.

(*b*) *DRY REACTION.*

(To be also practised on barium chloride.)

A platinum wire dipped first in hydrochloric acid and then in the salt, and held in the inner blowpipe or *Bunsen* flame, the outer flame is coloured yellowish-green.

(*c*) *SEPARATION.*

After removal of the metals of Groups 1, 2, and 3, the addition of ammonium carbonate determines the precipitation of Ba, Sr, and Ca as carbonates. This precipitate is dissolved in acetic acid, and on the addition of potassium chromate the barium precipitates, leaving the other two metals in solution.

II. STRONTIUM (Sr).

(*a*) *WET REACTIONS.*

(To be practised on strontium nitrate—$Sr2NO_3$.)

1. **$(NH_4)_2CO_3$** (*group reagent*) *in the presence of* **NH_4Cl** *and* **NH_4HO** gives a white precipitate of strontium carbonate—$SrCO_3$—soluble in dilute acetic acid.
2. **H_2SO_4**, or a soluble sulphate (preferably calcium sulphate), yields a white precipitate of strontium sulphate—$SrSO_4$—which only separates completely from dilute solutions on allowing them to stand in a warm place for some hours. It is insoluble in a boiling strong solution of ammonium sulphate rendered alkaline by ammonium hydrate (distinction from calcium sulphate).
3. The other reactions are similar to those of calcium.

(*b*) *DRY REACTION.*

(To be also practised on $Sr2NO_3$.)

A platinum wire moistened with hydrochloric acid, dipped in the substance and introduced into the *inner* blowpipe or *Bunsen* flame, colours the outer flame crimson.

(*c*) *SEPARATION.*

Strontium is precipitated in the 4th Group by ammonium carbonate, along with Ba and Ca, as already described. The precipitate having been dissolved in acetic acid, and the barium separated by potassium chromate, a small portion of the solution is tested by saturated solution of calcium sulphate:—if a precipitate be produced, the presence of strontium is evident. In this case some *very dilute* sulphuric acid is added, and the whole set aside in a warm place for some hours, when strontium sulphate separates. If the sulphuric

acid be added too strong, some $CaSO_4$ may also separate, and the precipitate should be digested for some time at a gentle heat, with a strong solution of ammonium sulphate containing a little ammonium hydrate, which dissolves $CaSO_4$ but leaves $SrSO_4$ insoluble.

III. CALCIUM (Ca).

(*a*) *WET REACTIONS.*

(To be practised on a solution of calcium chloride—$CaCl_2$.)

1. **$(NH_4)_2CO_3$** *in presence of* **NH_4Cl** *and* **NH_4HO** (*group reagent*) produces a white precipitate of calcium carbonate—$CaCO_3$—soluble in acetic acid and settling best on warming.
2. **$(NH_4)_2C_2O_4$** precipitates white calcium oxalate—CaC_2O_4—insoluble in acetic or oxalic acids, but soluble in hydrochloric acid.
3. **H_2SO_4** in strong solutions produces a precipitate of calcium sulphate, $CaSO_4$. Being slightly soluble in water, it does not form in dilute solutions, nor is it precipitated by a saturated solution of calcium sulphate (distinction from Ba and Sr). It is soluble in a boiling saturated solution of ammonium sulphate containing excess of ammonium hydrate, but quite insoluble in a mixture of two parts alcohol and one part water.
4. **Na_2HPO_4** produces a white precipitate of calcium phosphate soluble in acetic acid.

(*b*) *DRY REACTION.*

(To be practised on calcium carbonate—$CaCO_3$.)

A platinum wire moistened with hydrochloric acid, dipped in the substance and held in the inner blowpipe or *Bunsen* flame, colours the outer flame yellowish-red. This reaction is masked by the presence of Barium or Strontium.

(*c*) *SEPARATION.*

Calcium is precipitated in the 4th Group by ammonium carbonate (after removal of the metals of the 1st, 2nd, and 3rd groups) together with Ba and Sr. The precipitate is dissolved in acetic acid and the barium precipitated by potassium chromate. A portion of the solution is tested for strontium with $CaSO_4$, and if found absent, calcium is at once proved by adding ammonium oxalate to the remainder. If strontium be present, it is separated as already described by adding *very dilute* sulphuric acid, and the calcium is tested for in the filtrate by ammonium oxalate.

GROUP V.

Metals not precipitable either as sulphide, hydrate, or carbonate, including magnesium, the precipitation of which as hydrate or carbonate has been prevented by the presence of ammonium chloride.

I. MAGNESIUM (Mg).

(*a*) *WET REACTIONS.*

(To be practised on a solution of magnesium sulphate—$MgSO_4$.)

1. **Na_2HPO_4** *in the presence of* NH_4Cl *and* NH_4HO, produces a white crystalline precipitate of ammonium magnesium phosph[illegible] $MgNH_4PO_4$. It is slightly soluble in water, and s[illegible] water containing ammonium hydrate, but is hov[illegible]

in all acids. In very dilute solutions it forms only on cooling and shaking violently, or rubbing the inside of the tube with a glass rod.

2. **$(NH_4)_2HAsO_4$** produces a similar precipitate of $MgNH_4AsO_4$ possessing like features.
3. **KHO, NaHO,** and **NH_4HO** give precipitates of magnesium hydrate—Mg2HO—insoluble in excess, but soluble in the presence of ammonium salts. The alkaline carbonates (except ammonium carbonate) precipitate magnesium carbonate, also soluble in ammonium salts.
4. **Ca2HO** and **Ba2HO** produce a similar effect. Either of these reagents is useful for the separation of magnesium from all the alkalies except ammonium. The solution, which must contain no ammonium salts, is treated with excess of either lime or baryta water. The precipitated magnesium hydrate is then filtered out and excess of ammonium carbonate added, which precipitates in turn the excess of Ca or Ba employed and leaves K, Na, or Li in solution.

(*b*) *DRY REACTION.*

(To be practised on *magnesia*, B.P.—MgO.)

Heated on charcoal before the blowpipe, it becomes strongly incandescent, and leaves a white residue, which when moistened with a drop of solution of cobaltous nitrate—$Co2NO_3$—and again heated, becomes rose-coloured. This test is not however infallible.

(*c*) *SEPARATION.*

After separating the metals of the preceding groups by H_2S, NH_4Cl, and NH_4HO, NH_4HS and $(NH_4)_2CO_3$, all as already directed, the solution should be concentrated to about half its volume by evaporation and divided into a large and a small portion. The larger part is saved for the detection of the alkalies, and the smaller is made perfectly cold and treated with ammonium hydrate in excess, and then with disodium hydrogen phosphate, well shaken and set aside for some time, when the magnesium will separate as $MgNH_4PO_4$

II. LITHIUM (Li).

(*a*) *WET REACTIONS.*

(To be practised on a solution of lithium chloride, prepared by dissolving lithium carbonate in dilute hydrochloric acid.)

1. **Na_2HPO_4** in strong solutions produces a white precipitate of lithium phosphate—Li_3PO_4—on boiling only (distinction from Mg). It is soluble in hydrochloric acid, and reprecipitated by boiling with ammonium hydrate.
2. **Na_2CO_3**, and even NaHO, in very strong solutions yield the carbonate and hydrate respectively.
3. **$PtCl_4$** gives no precipitate (distinction from potassium).

(*b*) *DRY REACTION.*

(To be practised with lithium carbonate.)

A platinum wire, moistened with hydrochloric acid, dipped in the substance and held in the *inner* blowpipe or *Bunsen* flame, colours the outer flame *carmine red.* The presence of sodium disguises this reaction.

(*c*) *SEPARATION.*

Lithium is detected in the solution which is left after the precipitation of magnesium by disodium hydrogen phosphate. After filtering out the mag-

nesium precipitate a little more phosphate is added, and the whole evaporated to dryness. The residue is treated with a little *boiling* water, and any white insoluble matter may be taken as lithium phosphate, *provided it gives the characteristic carmine flame test above described.*

III. POTASSIUM (K).

WET REACTIONS.

(To be practised on solution of potassium carbonate treated with dilute HCl till effervescence ceases, forming potassium chloride—KCl.)

1. **$PtCl_4$**, in strong solutions, gives a yellow crystalline precipitate of potassium platino-chloride—K_2PtCl_6—soluble on great dilution, especially on warming, but insoluble in acids, alcohol, and ether.
2. **$H_2C_4H_4O_6$** throws down, from strong solutions only, a white crystalline precipitate of potassium hydrogen tartrate—$KHC_4H_4O_6$—soluble in much cold water, rather freely in hot water, readily in acids and in KHO or NaHO, and not formed unless the original solution be nearly neutral. Its separation is facilitated by stirring and shaking violently, in which case it settles quickly.
3. **H_2SiF_6** (*hydrofluosilicic acid*) yields white gelatinous potassium fluosilicate—K_2SiF_6—sparingly soluble in water.

DRY REACTION.

(To be practised on potassium carbonate—K_2CO_3.)

Dip a platinum wire, moistened with HCl, in the salt. Held in a *Bunsen* flame a *violet colour* is imparted. The masking effect of Na (*yellow*) is obviated by viewing the flame through indigo glass.

IV. SODIUM (Na).

WET REACTIONS.

(To be tested with solution of sodium chloride—NaCl.)

1. **$KSbO_3$** (*potassium metantimoniate*) gives a white granular precipitate of *sodium metantimoniate*—$NaSbO_3$—from strong solutions only, which must be neutral or alkaline. This precipitate is insoluble in alcohol.
2. **H_2SiF_6** gives a similar precipitate to that obtained with K salts in concentrated solutions only.

Sodium salts are, practically, all soluble in water, and there is no thoroughly trustworthy wet reaction which can be applied to detect small quantities. If we have a solution which gives no precipitate with any of the group reagents, but leaves, on evaporating, a fixed residue capable of imparting a *strong yellow colour* to the *Bunsen* flame (**dry reaction**), we may infer with certainty the presence of sodium.

SEPARATION.

When the filtrate from the precipitation of K by $PtCl_4$ is treated with H_2S, to separate the excess of Pt completely, filtered, and evaporated to dryness, a pure sodium salt is left.

SEPARATION OF POTASSIUM AND SODIUM FROM ALL OTHER METALS.

The portion saved for K and Na after separation of all other metals (see separation of Mg) is evaporated to dryness and heated till ammonium fumes cease

to be evolved, the residue is taken up with the smallest possible quantity of water and any insoluble matter filtered out. The flame test is applied to the solution; and if yellow, Na' is present. The test is then repeated, using a piece of indigo blue glass to cut off the yellow, and any violet indicates K, which is proved by adding platinic chloride and alcohol, and getting the yellow potassium platino-chloride.

V. AMMONIUM (NH_4).

WET REACTIONS.

(To be tested with solution of ammonium chloride—NH_4Cl.)

1. **$PtCl_4$** produces a heavy yellow precipitate of ammonium platino-chloride—$(NH_4)_2PtCl_6$—which, being rather soluble in water, is not formed in dilute solutions, unless alcohol, in which it is insoluble, be added in considerable quantity. When ignited, pure spongy platinum is left. This precipitate may be distinguished from that with K salts by adding, after ignition, a little water and $AgNO_3$, when no white precipitate of AgCl is formed (the K salt leaves KCl on being strongly heated).
2. **$H_2C_4H_4O_6$** yields ammonium hydrogen tartrate—$(NH_4)HC_4H_4O_6$—almost identical with $KHC_4H_4O_6$ in its properties. On ignition, however, the latter gives a black residue, which turns moistened red litmus paper *blue* (K_2CO_3 and C), the former leaving pure C without reaction.
3. **NaHO**, or **Ca2HO**, boiled with the solution causes the evolution of ammonia gas—NH_3. A glass rod dipped in HCl or $HC_2H_3O_2$ produces, when held over a mixture evolving NH_3, white clouds (solid NH_4 salts), and moist red litmus paper is turned blue.
4. **Nessler's Solution** (HgI_2 dissolved in KI and KHO added) gives a *yellow* or *brown colour* or a *brown precipitate* of $N(Hg_2)''I$ with all NH_4 salts. This reaction is extremely delicate, and the estimation of NH_4 in water is founded upon it.

DRY REACTIONS.

Ammonium salts volatilize (1) with decomposition, leaving a fixed acid (*e.g.*, phosphate); (2) with decomposition, leaving no residue whatever (*e.g.*, sulphate, nitrate); (3) without decomposition, when they are said to *sublime* (*e.g.*, chloride, bromide, etc.).

SEPARATION OF AMMONIUM FROM ALL OTHER METALS.

Ammonium is at once separated from any mixture by boiling with potassium hydrate in excess, when it is given off in the form of ammonia gas—NH_3.

CHAPTER III.

DETECTION AND SEPARATION OF ACIDULOUS RADICALS.

1. HYDROFLUORIC ACID and FLUORIDES.

(The test for fluorides undernoted may be practised on fluor spar—Ca F_2.)

Hydrofluoric Acid, or **Fluoric Acid,** is known,—

1. By its strongly acid reaction and corrosive power.
2. By the action upon glass from which it dissolves out silicic acid—Si O_2—thus roughening the surface and rendering it semi-opaque, or translucent, and white: a colourless gas, silicic fluoride—SiF_4—passing off.

Fluorides are detected as follows:—

The mineral or salt is finely powdered, and introduced into a leaden dish with a little sulphuric acid. A piece of glass, previously prepared by coating its surface with wax, and etching a few letters on the waxed side with the point of a pin, is placed over the dish, waxed side down. A gentle heat is then applied, but not sufficient to melt the wax, and the operation continued for some time. The glass is then taken off, and the wax removed from it; when, if fluorine was present, the letters written on the waxed surface will be found engraved upon it by the action of the hydrofluoric acid.

2. CHLORINE, HYDROCHLORIC ACID, and CHLORIDES.

Free Chlorine—Cl_2—may be detected,—

1. By its odour.
2. By turning paper dipped in solution of potassium iodide brown.
3. By bleaching a solution of indigo or litmus.

Hydrochloric Acid—HCl—may be recognised,—

1. By its acidity and odour of its fumes.
2. By producing dense white fumes when a rod dipped in ammonium hydrate is held over the mouth of the bottle.
3. By giving a curdy white precipitate of argentic chloride with argentic nitrate, instantly soluble in ammonium hydrate.

Chlorides give the following reactions (to be practised with any soluble chloride, say NaCl):—

1. Heated with sulphuric acid, they evolve white fumes of HCl.
2. Heated with H_2SO_4 and MnO_2 they evolve chlorine.
3. $AgNO_3$ *in the presence of* HNO_3 gives a white precipitate of argentic chloride—AgCl—insoluble in boiling nitric acid but instantly soluble in ammonium hydrate.
4. The solid substance mixed with $K_2Cr_2O_7$ and distilled with H_2SO_4 yields chloro-chromic acid—$CrCl_2O_2$—in red fumes which, when passed into dilute ammonium hydrate, colour it yellow, owing to the formation of ammonium chromate—$(NH_4)_2Cr$

The yellow should change readily to green on the addition of a few drops of sulphurous acid.

Insoluble Chlorides should be first boiled with strong sodium hydrate and the whole diluted and filtered. The chloride is then transferred to the sodium and is to be searched for in the filtrate by acidulating with nitric acid and adding argentic nitrate, as above described.

3. HYPOCHLOROUS ACID and HYPOCHLORITES.

Hypochlorous Acid is rarely met with, and it is hardly necessary to mention its reaction. However, the chlorine-like smell, the disengagement of chlorine when HCl is added, and the action of blue litmus, first reddening and almost instantly bleaching, are sufficiently distinctive. The odour, bleaching power, and action of HCl are properties possessed by **hypochlorites** in common with the acid itself. They are also indicated by their ready solubility in water.

4. CHLOROUS ACID and CHLORITES.

Chlorous Acid is a link between hypochlorous and chloric, and as such is worthy of a passing notice. It is energetic in entering into combination with hydrates, but does not act upon carbonates. Its solution has the properties of chlorine, but in an intensified degree, and is quickly decomposed by heat.

Chlorites are usually soluble in water, and only the silver and lead salts are of slight solubility. The former is not decomposed by boiling, and may thus be distinguished from the hypochlorite. Care must be taken that the heat does not reach 105° C., as the argentic chlorite then explodes.

5. CHLORIC ACID and CHLORATES.

Chloric Acid is a syrupy liquid readily decomposed by heat or reducing agents, often with explosive violence. It is colourless, strongly acid, and has no bleaching properties.

Chlorates (to be practised on potassium chlorate—$KClO_3$).

1. Heated on charcoal, they deflagrate.
2. Heated with strong sulphuric acid, they evolve chlorine peroxide—Cl_2O_4—which is yellow and explosive.
3. Their solutions yield no precipitate with argentic nitrate; but if a little of the solid be heated to redness, and the residue dissolved in water, a precipitate of argentic chloride is obtained. The same reduction from chlorate to chloride may also be effected by adding zinc and dilute sulphuric acid to the solution.

5a. SEPARATION OF CHLORATES AND CHLORIDES.

Add *excess* of argentic nitrate, filter out the argentic chloride formed, and then acidulate with sulphuric acid, and drop in a fragment of zinc, when, if a chlorate be present, a second precipitate of argentic chloride will form.

6. PERCHLORATES.

Are distinguished from chlorates—

1. By giving off perchloric acid, when heated with sulphuric acid, without explosion or evolution of chlorine peroxide.
2. Like chlorates, they require reduction to chlorides before giving a precipitate with argentic nitrate.

7. BROMINE, HYDROBROMIC ACID, and BROMIDES.

Bromine is distinguished,—

1. By its appearance—heavy, reddish-brown liquid, giving off reddish fumes of a very penetrating, unpleasant odour.
2. By turning starch paste yellow or pink.
3. When present in small quantity in solution, on adding a few drops of chloroform and shaking, an orange colour is imparted to that liquid, which sinks to the bottom of the aqueous solution.
4. By the bleaching power of its solution.

Hydrobromic Acid is known,—

By its acid reaction and the production of fumes of bromine with nitrous acid.

Bromides are all soluble in water, except the silver, mercurous, and lead salts; they are detected by the following characters (to be practised on potassium bromide—KBr):—

1. Heated with **strong sulphuric acid**, they evolve red vapours of bromine.
2. A similar effect is produced by **sulphuric acid** and **metallic dioxides**, such as PbO_2, MnO_2.
3. Mixed with **starch paste**, and a few drops of **chlorine water** carefully added, they give an orange colour (starch bromide).
4. Mixed in a long tube with **ether, chloroform, or carbon disulphide**, and a few drops of **chlorine water** added, the whole, when shaken well together, leaves a characteristic reddish-coloured stratum of free bromine, dissolved in the *menstruum* used In the case of ether, the stratum is visible on the top, while with the other two it is noticed at the bottom of the liquid in the tube.
5. With **argentic nitrate** they give a dirty-white precipitate of **argentic bromide**, insoluble in nitric acid, slowly soluble in ammonium hydrate.
6. Distilled with **potassium dichromate** and **sulphuric acid**, red fumes are evolved, which give no colour when passed into **ammonium hydrate**.

Insoluble Bromides should be first boiled with NaHO as described under insoluble chlorides.

8. DETECTION OF CHLORIDES IN THE PRESENCE OF BROMIDES.

(To be practised on a mixture of KCl and KBr.)

The solution is divided into two parts, in one of which the bromide is proved by the addition of chlorine water, and shaking up with chloroform. The second portion is evaporated to dryness, and the residue placed in a tube retort with a little potassium dichromate and sulphuric acid. Into the receiver is placed a little dilute ammonium hydrate, and distillation is proceeded with, when, if a chloride be present, the liquid in the receiver will be coloured yellow.

9. HYPOBROMOUS ACID and HYPOBROMITES.

These are very similar to hypochlorites, and react as follows:—

1. They decompose by heat, leaving a bromide:
2. On boiling with an alkali, a mixture of bro
3. The acid itself is straw-yellow in colour, a

10. BROMIC ACID and BROMATES.

These are recognised—

1. By deflagrating on charcoal, leaving the corresponding bromide.
2. By liberating bromine on the addition of dilute sulphurous acid.

11. IODINE, HYDRIODIC ACID, and IODIDES.

Iodine is readily known by its glistening black scales, its odour, the violet vapour on heating, and the production of blue iodide of starch on adding a solution to starch paste.

Hydriodic Acid, in the gaseous state, is known by the formation of a brown colour on holding paper moistened with chlorine water (blue if also dipped in starch paste) over a tube in which it is being evolved. The solution decomposes on exposure to the air, becoming yellow or brown on account of the separation of iodine. Thus, if the solution be colourless at first, acid in reaction, and giving no effect with starch paste, but producing a blue on exposure to the air, or more rapidly on adding HNO_3 or Cl water, HI may be inferred with certainty.

Iodides are readily known by the following reactions (which may be practised on solution of potassium iodide, KI) :—

1. The light yellow precipitate of argentic iodide—AgI—formed when a solution (containing alkaline metals only) is added to **argentic nitrate** dissolved in water. The precipitate, when freed from the supernatant liquid, does not dissolve in hot HNO_3 and is practically insoluble in ammonium hydrate, being thus distinguished from a chloride.
2. A *neutral* solution (produced, if alkaline in the first place, by the cautious addition of dilute HNO_3; if acid, by dropping in KHO solution until test-paper is unaffected) gives with one part of **cupric sulphate**—$CuSO_4$—and three parts, or rather less, of **ferrous sulphate**—$FeSO_4$—dissolved in a little water, a greyish precipitate of **cuprous iodide**—$(Cu_2)''I'_2$.

   The same precipitate is produced if **sulphurous acid**—H_2SO_3—be used with the cupric sulphate instead of ferrous sulphate.
3. **Palladious Chloride**—$PdCl_2$—or **palladious nitrate**—$Pd2(NO_3)$—gives a black precipitate of **palladious iodide**—PdI_2—decomposed somewhat below the temperature of boiling mercury, iodine being evolved, and the metal left. This is a very expensive but efficient separation.
4. **Mucilage of Starch** and **nitrous acid** or **chlorine water** (if not added too plentifully), produces **blue** iodide of starch, decomposed by heat but re-formed on cooling; also destroyed by excess of Cl (iodine tri-chloride—ICl_3—being produced). The **nitrous acid** may be replaced by **potassium nitrite**—KNO_2—and dilute H_2SO_4, the HNO_2 then being set free in the solution. An iodide treated with strong H_2SO_4 yields HI at first; but this acting on the excess of acid, is transformed into free I, the H_2SO_4 at the same time being reduced by the hydrogen to sulphurous acid—H_2SO_3—or even to sulphuretted hydrogen —H_2S.
5. When **mercuric chloride**—$HgCl_2$—in aqueous solution, is cautiously dropped into a liquid containing an iodide, a stage is reached at which a permanent precipitate of red mercuric iodide—HgI_2—is produced. The reaction is not reliable unless great

care be taken, as too rapid or insufficient addition of the $HgCl_2$ may either dissolve the precipitate or fail to form it. If actually produced, however, its colour and insolubility indicate iodine with certainty, since Cl, Br, and Cy are colourless and soluble when combined with mercury (ic).

6. **Plumbic Nitrate** or **Acetate**—$Pb2(NO_3)$—or $Pb(C_2H_3O_2)_2$, throw down yellow PbI_2 from cold solutions. This precipitate is soluble in hot water, and dissolves slightly even at ordinary temperatures; consequently the test cannot be relied on to give any effect in weak solutions.

12. DETECTION OF BROMIDES IN THE PRESENCE OF IODIDES.

(Practise on a mixture of KBr and KI.)

Add to the solution a very small quantity of starch paste and then a drop or two of chlorine water, when a blue colour will be produced proving the iodide. Continue to add more chlorine water until this blue is entirely discharged and then shake up with chloroform, when, if a bromide be present, the characteristic golden colour will be communicated to the chloroform.

13. DETECTION OF CHLORIDES IN THE PRESENCE OF IODIDES.

(Practise on a mixture of KCl, KBr, and KI.)

Add excess of argentic nitrate, warm, pour off the supernatant liquid, wash with warm water, and shake up the precipitate in dilute solution of ammonium hydrate (1 in 3). The argentic iodide will remain insoluble, while the chloride will dissolve and may be detected in the solution after filtration by reprecipitation with excess of nitric acid. As argentic iodide is not *absolutely* insoluble in ammonium hydrate, a mere cloud on adding the nitric acid is to be disregarded. This test is only accurate in the ensured absence of a bromide, proved as above directed (see 12). If a bromide is present, the chloride can only be proved by the distillation with potassium dichromate and sulphuric acid (see 8).

14. SEPARATION OF AN IODIDE FROM A BROMIDE AND CHLORIDE.

(Practise on a mixture of KCl, KBr, and KI.)

1. Add to the solution a mixture of one part **cupric sulphate** and three parts **ferrous sulphate**, or mix the solution with excess of **cupric sulphate** and drop in **sulphurous acid** till precipitation ceases. The iodide will separate as cuprous iodide—Cu_2I_2—leaving the bromide and chloride in solution. Unless carefully done, this separation is not absolutely accurate.
2. Add to the solution palladious nitrate until precipitation ceases. Filter out the palladious iodide which separates and pass sulphuretted hydrogen through the liquid to remove excess of palladium and again filter. Boil to expel the excess of H_2S, and the bromide and chloride remain in solution.

15. IODIC ACID and IODATES.

The acid is a crystalline solid, breaking up by heat into oxygen and violet vapours of iodine. Iodates are known,—

1. By giving a blue with starch paste on the additi[illegible] acid.

2. By yielding a precipitate of ferric oxy-iodate on adding ferric chloride.

15a. DETECTION OF AN IODATE IN AN IODIDE.

(Practise on a solution of iodine in heated potassium hydrate—$KI + KIO_3$.)

When excess of tartaric acid is added to potassium iodate, iodic acid is set free; and when the same acid is added to potassium iodide, hydriodic acid is set free, and potassium hydro-tartrate formed. Thus:

$$5KI + KIO_3 + 6H_2C_4H_4O_6 = 5HI + HIO_3 + 6KHC_4H_4O_6.$$

If these acids be thus liberated together, they immediately decompose, forming water and free iodine:

$$5HI + HIO_3 = 3I_2 + 3H_2O.$$

If therefore starch paste and tartaric acid be added to pure potassium iodide no coloration takes place, because only hydriodic acid is liberated; but if the sample contains potassium iodate, an immediate production of free iodine ensues, which turns the starch blue.

16. PERIODIC ACID and PERIODATES.

Periodic Acid is known,—

1. By its strongly acid deliquescent crystals, decomposed by heat into iodic anhydride—I_2O_3—and ultimately into I and O.
2. By the production of I, by the action of organic and other reducing agents.

Periodates are distinguished,—

1. By precipitating with **barium chloride**—$BaCl_2$—in a neutral solution and digesting in **ammonium carbonate** to which some NH_4HO has been added. The periodate is not decomposed. Iodates leave barium carbonate, which when washed dissolves in acid with effervescence.
2. By adding $Hg2NO_3$ and treating the yellowish precipitate with $SnCl_2$. It turns green, Hg_2I_2 being produced.

17. WATER and HYDRATES.

Water is recognised,—

1. By its absolute neutrality to test-paper.
2. By its evaporating without residue, fumes, or odour of any kind.
3. By its turning white anhydrous cupric sulphate blue.
4. By its yielding pure hydrogen when boiled and the steam passed slowly over *ferrum redactum*, B.P., heated to bright redness in an iron tube.
5. By its undergoing electrolysis, and yielding hydrogen at the negative and oxygen at the positive electrode.

The soluble Hydrates, viz., KHO, NaHO, LiHO, Ba2HO, Sr2HO, and Ca2HO are known,—

1. By being more or less soluble in cold water, yielding solutions which are strongly alkaline to test-paper.
2. By dissolving in hydrochloric acid without effervescence and without smell.
3. By giving a brownish-black precipitate of argentic oxide—Ag_2O—with argentic nitrate.

The **insoluble Hydrates** are recognised,—

By giving off steam when heated in a dry test-tube and leaving a residue which behaves like the corresponding oxide.

18. OXIDES.

All oxides are insoluble in water. Those of K, Na, Li, Ba, Sr, and Ca, when placed in contact with that liquid, unite with it to form hydrates, which dissolve with a greater or less degree of readiness and give the characters of the soluble hydrates already mentioned.

Normal Oxides can only be recognised by negative results, such as:—

1. Heated alone, they are not changed; except argentic oxide, which leaves the metal, and mercuric oxide, which volatilizes and breaks up into the metal and oxygen.
2. They are insoluble in water (exceptions K, Na, Li, Ca, Ba, and Sr, converted into soluble hydrates) but soluble in hydrochloric or nitric acid without effervescence and without smell.
3. After dissolving and removing the metal by H_2S or Na_2CO_3 as most convenient, no acidulous radical other than that of the acid used to dissolve is found.
4. Boiled with strong NaHO and filtered, or fused with $KNaCO_3$ and digested with water, the solution gives no reaction for any acid radical except the soluble hydrate or carbonate employed.

Peroxides, on account of their containing an excess of oxygen, differ from normal oxides,—

1. By giving off oxygen when strongly heated.
2. By evolving chlorine when heated with hydrochloric acid.

19. SULPHUR, HYDROSULPHURIC ACID, and SULPHIDES.

Ordinary Sulphur is recognised,—

1. By its burning entirely away with a pale blue flame, and evolving sulphurous anhydride.
2. By its insolubility in all ordinary menstrua, such as water, alcohol, and ether, but dissolving readily in carbon disulphide.
3. When slowly heated in a tube, it first melts, then thickens, then melts again, and finally boils, the vapour taking fire and forming sulphurous anhydride.

Precipitated Sulphur possesses the above characters and is specially distinguished from ordinary sulphur by being quite amorphous under the microscope, while the latter is crystalline.

Hydrosulphuric Acid (sulphuretted hydrogen) is known,—

1. By being a colourless gas with a disgusting odour of rotten eggs and inflammable, burning in the air to produce sulphurous acid.
2. By turning a piece of paper black, which has been moistened with solution of plumbic acetate and held over the mouth of the tube or jet from which it issues.

Normal Sulphides are divisible into five classes:—

1. Soluble in water, including the sulphides of K, Na, NI and Mg.

2. Insoluble in water, but readily soluble in dilute hydrochloric acid, including those of Fe, Mn, Zn.
3. Insoluble in dilute, but soluble in strong boiling hydrochloric acid, including the sulphides of Ni, Co, Sb, and Sn (PbS is also slightly affected, but separates on cooling, as chloride).
4. Insoluble in hydrochloric acid, but attacked by strong heated nitric acid, being converted wholly or partially into sulphates. These include the sulphides of Pb, Ag, Bi, Cu (arsenious sulphide is slowly affected).
5. Not dissolved by any single acid, but converted into a soluble sulphate by the action of nitro-hydrochloric acid, or hydrochloric acid and potassium chlorate; including those of Hg, As, Au, and Pt.

Sulphides soluble in water or in hydrochloric acid are recognised,—

1. By giving off sulphuretted hydrogen when heated with that acid, which gives the smell and reactions already noted.
2. Soluble sulphides precipitate solutions of lead and cadmium, black and yellow respectively.
3. Soluble sulphides give a purple colour with sodium nitroprusside only after the addition of a soluble hydrate.

Sulphides insoluble in hydrochloric acid are best detected,—

1. By heating with strong nitric or nitro-hydrochloric acid, diluting the solution, and testing for a *sulphate* with barium chloride (see 24).
2. By fusion with $KNaCO_3$ and KNO_3, digesting the residue in water, filtering and testing the solution for a *sulphate* formed by the oxidizing action of the potassium nitrate.
3. Mix a little with sodium carbonate and borax, and heat on charcoal before the blowpipe. Remove the mass thus obtained, place it on a clean silver coin, and moisten with a drop of distilled water; when, owing to the formation during ignition of sodium sulphide —Na_2S—a black stain of argentic sulphide—Ag_2S—will be produced.

Polysulphides as commonly met with are those of the alkalies, and are soluble in water. They are known,—

1. By the deep yellow or orange colour of their solutions.
2. By evolving sulphuretted hydrogen *accompanied by a deposit of sulphur* when treated with hydrochloric or dilute sulphuric acids.

The polysulphides which are insoluble in hydrochloric acid, such as iron pyrites—FeS_2—copper pyrites—$Fe_2Cu_2S_4$—etc., are best proved by fusion and conversion into sulphate. They may, however, be recognised by heating with hydrochloric acid and zinc, when the excess of sulphur will pass off as H_2S, leaving the normal sulphide.

20. DETECTION OF A SOLUBLE SULPHIDE IN PRESENCE OF A SULPHITE AND A SULPHATE.

Pour the solution on a little cadmium carbonate—$CdCO_3$—filter, and treat the insoluble matter with acetic acid to remove any unacted-upon cadmium carbonate. If a sulphide have been present, a yellow residue of cadmium sulphide will remain insoluble in the acetic acid, while cadmium sulphite and sulphate will be found in the first filtrate, if these two radicals were present separation of sulphites and sulphates).

21. THIOSULPHURIC ACID and THIOSULPHATES (Hyposulphites).

The acid is not known in the free state; but its salts, commonly known as hyposulphites, are usually soluble in water, and exhibit the following characters:—

1. With either dilute or strong HCl and H_2SO_4, they yield SO_2 gas and a *yellow* deposit of S (*distinction from sulphides, polysulphides, and sulphites*).
2. $AgNO_3$ gives no precipitate at first, owing to excess of a hyposulphite dissolving argentic hyposulphite—$Ag_2S_2O_3$—but on continuing the addition, this $Ag_2S_2O_3$ is precipitated of a *white* colour. The salt splits up spontaneously, becoming yellow, brown, and lastly black, and being changed completely into argentic sulphide—Ag_2S. The same decomposition of the precipitate occurs on substituting $HgNO_3$ or $Pb2NO_3$ for $AgNO_3$; and in all three cases heat accelerates the action, and H_2SO_4 is the by-product.
3. Fe_2Cl_6, Na_2OCl_2, and Cl water convert hyposulphites into sulphates, even without applying heat.

$$Na_2S_2O_3 + H_2O + 4Na_2OCl_2 = 2NaHSO_4 + 8NaCl.$$

The first produces a reddish-violet colour, and this gradually disappears as $FeCl_2$ is formed. (*This colour is not produced by sulphites.*)

4. HCl and dilute H_2SO_4 evolve H_2S *when zinc is dropped in*. The reaction is,—

$$4\ Zn + 10HCl + Na_2S_2O_3 = 4ZnCl_2 + 2NaCl + 3H_2O + 2H_2S.$$

22. SEPARATION OF THIOSULPHATES FROM SULPHIDES.

Having obtained a good preliminary idea by heating with $H_2\ SO_4$, add to a portion of the original solution—$ZnSO_4$—in excess, and filter.

(*a*) Precipitate white, and soluble in HCl, with smell of H_2S

= **Sulphides.**

(*β*) A portion of filtrate heated with H_2SO_4 deposits S and smells of SO_2; and another portion added to a drop or two of ammonio-cupric sulphate instantly causes decolorization

= **Hyposulphites.**

23. SULPHUROUS ACID and SULPHITES.

Sulphurous acid in solution is recognised,—

1. By its pungent odour of burning sulphur.
2. By adding barium chloride in excess, filtering out any precipitate of barium sulphate which may form (owing to the fact that all samples of the ordinary acid contain sulphuric acid), and then adding chlorine water and getting another copious white precipitate of barium sulphate owing to the conversion of the sulphurous into sulphuric acid by the oxidizing action of the chlorine water, thus:—

$$H_2SO_3 + BaCl_2 + Cl_2 + H_2O = BaSO_4 + 4HCl.$$

3. Treated with zinc and hydrochloric acid, it evolves sulphuretted hydrogen, thus:—

$$3Zn + 6HCl + H_2SO_3 = 3ZnCl_2 + H_2S + 3H_2O.$$

4. When a solution of iodine is dropped into the liquid, its colour is discharged, owing to its conversion into hydriodic acid by the hydrogen of the water, the oxygen of which passes at the same time to the sulphurous acid, forming sulphuric acid.

$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$

Sulphites are known by the following characteristics :—

1. All except the alkaline sulphites are sparingly soluble in water.
2. When heated with sulphuric acid they evolve sulphurous anhydride, *without deposit of sulphur.*
3. Acted on with zinc and hydrochloric acid, they evolve sulphuretted hydrogen, which blackens a piece of paper moistened with plumbic acetate and held over the mouth of the test-tube.
4. A salt of silver, mercury, or lead, produces a precipitate, which on heating turns dark, owing to the formation of a sulphide and free sulphuric acid.
5. By boiling with barium chloride and chlorine water or nitric acid, barium sulphate is produced, and precipitates.
6. The acid gas—SO_2—combines directly with peroxides to form sulphates. For instance :—

$$PbO_2 + SO_2 = PbSO_4.$$

This reaction is utilized in gas analysis, to separate SO_2 from a gaseous mixture.

7. $K_2Cr_2O_7$ and HCl give a beautiful green coloration of *chromic sulphate* or *chloride.* This test is very delicate, but by itself is not conclusive.

24 SULPHURIC ACID and SULPHATES.

The acid is detected as subjoined :—

1. By its appearance. A heavy, oily, odourless, and nearly colourless liquid, powerfully acid and corrosive.
2. By its charring effect. This is made evident when the strong acid is dropped upon white paper, wood, etc., or when the dilute acid is evaporated in a basin containing a little white sugar. The carbonization is due to the power the acid has of abstracting the elements of water from organic bodies.
3. By liberating an explosive gas from $KClO_3$ when heated with it. The test is not available with dilute acid.

Sulphates are soluble in water, with the exception of *basic sulphates* (soluble in acids) and $BaSO_4$, $SrSO_4$, $CaSO_4$, and $PbSO_4$. (Ag_2SO_4 is only slightly soluble.) When those insoluble in dilute acids are required to be analysed, they are decomposed either by boiling with potassium or sodium hydrates or by ignition with $KNaCO_3$, the latter being preferable. The sulphate radical, being brought into combination with K or Na to form a soluble sulphate, is to be tested for in the filtrate after boiling with water. Sulphates are recognised by the following characters :—

1. **$BaCl_2$** or $Ba2NO_3$ produces a white precipitate of barium sulphate —Ba SO_4—insoluble in boiling water and also (after washing to remove excess of $BaCl_2$) in boiling nitric acid. This washing is necessary, as the addition of a strong acid to a solution of barium chloride often causes the reagent to crystallize out, and this is then mistaken by the student for a true precipitate of sulphate.

2. The addition of a soluble salt of lead or strontium also causes the formation of insoluble sulphates; but these reactions are never in practice used, the barium chloride being at once the most delicate and serviceable reagent.
3. Heated with a little Na_2CO_3 on charcoal in the inner blowpipe flame, sulphates are reduced to sulphides, and the residue placed on a clean silver coin and moistened with water, leaves a black stain.

25. SEPARATION of SULPHIDES, SULPHITES, and SULPHATES.

Pour the solution on an excess of cadmium carbonate, digest at a gentle heat, filter, and examine the precipitate for a sulphide as already directed (19). The filtrate, which may contain the sulphite and sulphate, is precipitated by barium chloride, the insoluble precipitate filtered out and boiled with a little hydrochloric acid, which will dissolve the barium sulphite with evolution of sulphurous anhydride—SO_2—and leave the barium sulphate insoluble.

26. CARBON, CARBONIC ACID, and CARBONATES.

Carbon is known:—

1. By its black colour and the production of a gas when burnt, which is odourless, so heavy that it can be poured from one vessel to another, and causes a white precipitate when passed into solution of calcium hydrate.
2. By its capability of removing many vegetable colouring matters from their solutions.

Carbonic Acid is not known in the free state, splitting up into **carbonic anhydride**—CO_2—and water. CO_2 is recognised,—

1. By being odourless and giving white insoluble $CaCO_3$ (or $BaCO_3$) when passed into a solution of Ca2HO (or Ba2HO).
2. By turning blue litmus purple or wine-red, the original tint being restored by heat, the CO_2 escaping.

Carbonates are mostly insoluble in water, the alkaline carbonates alone dissolving. $CaCO_3$, $SrCO_3$, $BaCO_3$ and $MgCO_3$ (also $MnCO_3$ and $FeCO_3$) dissolve in water containing CO_2 (especially under pressure) forming bicarbonates or hydrogen carbonates, from which CO_2 passes off on boiling. All carbonates give off CO_2 on ignition, except K_2CO_3 and Na_2CO_3. A white heat is needed to decompose $BaCO_3$ and $SrCO_3$. A few carbonates yield the metal on heating, but the majority leave the oxide. Their recognition depends upon,—

1. Effervescing with a solution of almost any acid (H_2S and HCy excepted), organic or inorganic, and giving off an odourless gas—CO_2.
2. When the gas given off is poured or passed into a solution of calcium hydrate, a white precipitate of $CaCO_3$ falls, which dissolves on continuing to add CO_2. When the gas given off has the odour of H_2S or SO_2, either of these may be removed by passing through K_2CrO_4 and HCl, which is rendered green, and the unacted-upon CO_2 is allowed to pass into calcium hydrate solution as before.

27. BORIC ACID and BORATES.

Boric (*or* Boracic) Acid—H_3BO_3— is a common s
under :—

1. It is a white crystalline solid, giving off water on being heated and leaving the *anhydride*—B_2O_3.
2. When warmed with alcohol, a *green flame* is produced on applying a light to the latter.
3. When dissolved in hot water and a piece of turmeric paper dipped in the solution, the yellow colour is unaffected; but upon drying the paper it becomes brownish-red.

All **borates** dissolve in dilute acids, but few in water, and when decomposed by hot acids, let fall crystalline boric acid on cooling, which answers to the above characters.

The presence of soluble **borates** is detected by the following tests:—

1. They give, on heating with **calcium chloride**, rendered slightly alkaline with ammonium hydrate, a white precipitate of calcium borate, soluble in acetic acid, and so distinguished from oxalate.
2. On rendering the solution *just acid* with hydrochloric acid, and then dipping in a piece of turmeric paper, and drying the same after immersion at a *gentle* heat it will be turned red.
3. Besides these two tests, which are in themselves, taken together, quite conclusive, borates give a precipitate with argentic nitrate soluble in nitric acid.
4. When a little of the solid borate is moistened, first with a drop of sulphuric acid and then with about a drachm of spirit of wine, the alcoholic solution of boric acid so obtained burns with a bright green flame.
5. When $KHSO_4$ (potassium hydrogen sulphate) is heated with a borate in the blowpipe flame on platinum wire, the flame is tinged *green*.

28. SILICIC ACID and SILICATES.

The acid H_4SiO_4 is scarcely ever met with, and we have practically to deal with the anhydride—SiO_2—which is totally insoluble in water and dilute acids, the acid dissolving slightly in both. SiO_2 is characterized,—

1. By its infusibility when heated.
2. By its insolubility in water and all acids except HF.
3. By forming, when heated with H_2SO_4 and CaF_2 in a leaden vessel, *gaseous silicic fluoride*—SiF_4—which deposits the acid—H_4SiO_4—and forms *hydro-fluosilicic* acid—H_2SiF_6—and HF, in contact with moisture.

Silicates are not as a rule soluble in water, K_4SiO_4 and Na_4SiO_4 being the only ones thus affected, especially when much KHO or NaHO is present. Many of them do not dissolve in strong acids (a few are decomposed by hot H_2SO_4, but by no other acid), but all are split up by the action of gaseous hydrofluoric acid or a mixture of CaF_2 and H_2SO_4.

1. On adding HCl to a soluble silicate H_4SiO_4 falls as a gelatinous,—scarcely visible,—precipitate, slightly soluble in water. On evaporating to dryness and heating to 280° or 300° F., the addition of a little HCl and water always fail to affect the SiO_2 which is left as a white gritty residue.
2. NH_4Cl precipitates H_4SiO_4 from a soluble silicate.
3. Silicic anhydride is separated from all acidulous and basylous radicals by fusing the finely powdered insoluble silicate with Na_2CO_3 (or *fusion mixture*), in a platinum crucible; boiling with water, filtering, evaporating nearly to dryness, adding dilute HCl until the whole is acid, re-evaporating, moistening with

water, and when dry heating to 280° or 300° F. On adding a little HCl, SiO_2 alone remains insoluble.

29. SEPARATION OF SILICIC ANHYDRIDE (SILICA) FROM ALL OTHER ACIDS.

Fuse the substance with a large excess of $KNaCO_3$ in a platinum crucible, and when all action has ceased, cool, and boil the residue with water. The silica passes into solution with the other acid radicals, and the metals are left as oxides. Acidulate the solution with hydrochloric acid, evaporate to dryness, and heat the residue to 280° Fah., and maintain the heat for some time. Drench the residue with strong hydrochloric acid, then add water, and boil, when the silica will alone remain insoluble.

30. HYDROFLUOSILICIC ACID (H_2SiF_6).

This acid is only known in solution.

1. It is very acid, and dissolves metals with the evolution of hydrogen, forming silico-fluorides which decompose by heat, leaving fluorides, and giving off silicon fluoride—SiF_4.
2. It gives off hydrofluoric acid when evaporated, and should not, therefore, be heated in glass vessels, as they would be etched.
3. The majority of silico-fluorides are soluble, the exceptions being K_2SiF_6, $BaSiF_6$, and Na_2SiF_6, which are insoluble, especially in presence of a little alcohol.
4. It does not precipitate strontium salts, even from strong solutions, but throws down $BaSiF_6$ on adding $BaCl_2$ and alcohol, as a *white translucent crystalline precipitate.*
5. Potassium salts throw down *gelatinous* K_2SiF_6.

31. NITROUS ACID and NITRITES.

Nitrous Acid (so called commercially) is nitric acid containing nitrous anhydride. It is yellowish in colour, and evolves reddish fumes.

Nitrites are all soluble in water, the least so being argentic nitrite. They are known as follows :—

1. They give red fumes when treated with strong sulphuric acid, because the nitrous acid is thereby decomposed into nitric acid, and nitric oxide which then fumes in contact with the air.
2. They give an instantaneous blue colour with potassium iodide and starch paste on the addition of a few drops of dilute sulphuric acid. The sulphuric acid liberates hydriodic acid from the iodide, and nitrous acid from the nitrite ; the hydriodic acid is decomposed by the nitrous acid into iodine, water, and nitric oxide :

$$2HNO_2 + 2HI = I_2 + 2H_2O + 2NO.$$

[*Nitrates*, it must be remembered, would give frequently a similar re-reaction after standing, through the possible reduction of some portion of their nitric acid to nitrous acid ; so that unless the reaction appears instantly, and is confirmed by others, it is not safe to rely upon it as a test.]

3. They give a dark brown colour with ferrous sulphate *without the previous addition of sulphuric acid, as required by nitrates.*
4. Potassium dichromate in solution is converted into a green liquid by the addition of a nitrite and an acid. These two latter

stances also reduce an auric solution, forming a precipitate of the metal, possessing a dark colour.

32. DETECTION OF A NITRITE IN THE PRESENCE OF A NITRATE.

Add a little potassium iodide and starch paste, then introduce a small pinch of powdered metallic zinc, and lastly acidulate with acetic acid, when, if a nitrite be present, a blue colour will be produced, due to the liberation of iodine. This test is often a very necessary one when dealing with drinking water, the presence in which of nitrites, derived from the oxidation of comparatively recent organic contamination, is a dangerous indication.

33. NITRIC ACID and NITRATES.

Nitric Acid is strongly acid and corrosive, fumes in the air, and readily dissolves most metals. It may be at once recognised by the following characters:—

1. When poured on a piece of copper foil, and a piece of white paper held behind the test-tube, it is observed to be filled with orange-red fumes of nitric peroxide—N_2O_4.
2. When dropped on a piece of quill in a basin, or if the solution be weak when evaporated in contact with the quill, the latter is stained yellow. This stain is intensified to orange on adding an alkali, and is not discharged by warming, both of which decolorize the corresponding stains produced by iodine and bromine.
3. Dropped on a few crystals of brucine, a deep red colour is produced.

Nitrates are characterized by the following properties:—

1. All nitrates are soluble in water, especially when slightly acidulated with nitric acid. The nitrates of the alkalies are only decomposed by a very high temperature, but most of the nitrates of the heavy metals, such as copper, mercury, and lead, when heated are readily decomposed, leaving a residue of oxide. Argentic nitrate, however, when heated leaves metallic silver.
2. When heated with sulphuric acid they evolve pungent fumes of nitric acid.
3. When heated with sulphuric acid and a piece of copper wire, they produce red fumes of nitric peroxide (caused by the union of the nitric oxide evolved with the oxygen of the air).
4. When mixed with a solution of ferrous sulphate in the presence of sulphuric acid, a black coloration is produced, which is due to the production of nitric oxide, and its absorption by the ferrous salt. On heating, the colour disappears, and the *ferrous* is changed to the *ferric* sulphate. There are two ways of applying this test.

(*a*) Place a drop or two of the suspected solution on a white porcelain slab or crucible lid, and having added a drop of strong sulphuric acid, put a small and clean crystal of the ferrous sulphate in the liquid, when a black ring will gradually form round the crystal.

(*b*) Place the suspected solution in a tube, and having added some strong solution of ferrous sulphate, cautiously pour some strong sulphuric acid down the side of the tube, so that it sinks to the bottom by reason of its great gravity without mixing with the fluid. If nitric acid be present, a dark line will be formed at the junction of the two liquids.

5. Treated with sulphuric acid, and a few drops of indigo sulphate added, the blue colour of the latter is destroyed, being changed to yellow (not characteristic).
6. The most delicate test for nitrates is, however, phenyl-sulphuric acid. This reagent is prepared by dissolving one part of carbolic acid in four parts of strong sulphuric acid, and then diluting with two parts of water. A few drops of the solution to be tested are evaporated to dryness on a porcelain crucible lid over the water bath, and while still over the bath a drop of the reagent is added, when a reddish colour is immediately produced, owing to the formation of nitro-phenol.

34. DETECTION OF FREE NITRIC ACID IN THE PRESENCE OF A NITRATE.

Digest with excess of barium carbonate; filter, and add to the filtrate some dilute sulphuric acid, when, if the free acid were present, a precipitate of barium sulphate will be produced. This test is only good in the ensured absence of sulphates and of any other acid capable of dissolving barium carbonate. It will also serve for detecting free hydrochloric and acetic acids in presence of their salts.

35. DETECTION OF A NITRATE IN THE PRESENCE OF AN IODIDE.

The fact that the addition of strong sulphuric acid liberates iodine, renders the proof of a nitrate by the ordinary iron process doubtful in the presence of iodides and bromides. In this case warm with a little zinc amalgam and add a little acetic acid and starch paste, when the nitrate, being reduced to nitrite, will cause the liberation of iodine, and colour the starch paste blue.

Another process is, to evaporate to dryness with excess of potassium hydrate and a little sugar, and then fuse the residue, when, if a nitrate be present, ammonia gas—NH_3—will be given off; and will turn moistened red litmus paper blue. The first process is as a rule the better of the two, and zinc amalgam is easily made with a drop of mercury and a fragment of granulated zinc.

A third process is, to boil with stannous chloride and a large excess of hydrochloric acid, which will produce ammonium chloride from a nitrate; and by boiling the liquid with excess of potassium hydrate, the ammonia gas may be evolved.

36. SEPARATION OF CHLORIDES, IODIDES, AND BROMIDES FROM NITRATES.

Digest with argentic sulphate, which will precipitate the hallogens as silver salts, and leave the nitrate in solution.

37. CYANOGEN, HYDROCYANIC ACID, and CYANIDES.

Cyanogen is a colourless gas, which is recognised,—
1. By its odour of bitter almonds.
2. By its burning in the air with a peach-blossom coloured flame, producing carbonic anhydride and nitrogen.

Hydrocyanic Acid is volatile, soluble in water, and possesses a characteristic faint sickly odour. Its reddening action on litmus paper is very transient. Its tests are four in number, as follows:—
1. *The Silver Test.*—Argentic nitrate added

acid, gives a curdy white precipitate of argentic cyanide. The precipitate is soluble in ammonium hydrate and in strong boiling nitric acid, but not in dilute nitric acid; nor does it blacken on exposure to the light. Dried and heated it darkens, evolving half its cyanogen, leaving a mixture of silver and argentic paracyanide. During the action effervescence is observed, and a bright glow seems suddenly to pass through the mass.

2. *Scheele's Iron Test.*—An excess of solution of potassium hydrate is mixed with the solution. To this a mixture of a ferrous and a ferric salt is added, and the whole acidulated with hydrochloric acid. If hydrocyanic acid be present, *Prussian blue* will be formed.

The explanation of the test is as follows (according to Gerhardt's view).

(1) The hydrocyanic acid and the potassium hydrate form potassium cyanide.
(2) The addition of the ferrous salt produces ferrous cyanide.
(3) This reacting with the excess of alkali forms potassium ferrocyanide.
(4) On the addition of the ferric salt, it is at first precipitated by the excess of alkali, as ferric hydrate, which on acidulation dissolves to ferric chloride, forming ferric ferrocyanide (Prussian blue).

$$(1)\ 6HCy + 6KHO = 6KCy + 6H_2O.$$
$$(2)\ 6KCy + 3FeCl_2 = 3FeCy_2 + 6KCl.$$
$$(3)\ 3FeCy_2 + 4KHO = K_4FeCy_6 + 2Fe2HO.$$
$$(4)\ 3K_4FeCy_6 + 2Fe_2Cl_6 = (Fe_2)_2 3FeCy_6 + 12KCl.$$

Or the whole may be shown in one equation, thus, which is quite sufficient:—

$$18KCy + 3FeCl_2 + 2Fe_2Cl_6 = (Fe_2)_2 3FeCy_6 + 18KCl.$$

3. *The Sulphur Test.*—A few drops of *yellow* ammonium sulphydrate is added to a solution of hydrocyanic acid, and the whole evaporated to dryness at a very gentle heat, with the addition of a drop of ammonium hydrate. A residue is thus obtained which strikes a blood-red colour with ferric chloride, not dischargeable by hydrochloric acid, but at once bleached by solution of mercuric chloride. This colour is due to the formation of ammonium sulphocyanide (which takes place when an alkaline sulphide, containing excess of sulphur, is brought into contact with cyanogen)—

$$2HCy + (NH_4)_2S + S_2 = 2NH_4CyS + H_2S.$$

and subsequent production of red ferric sulphocyanide.

4. *Schönbein's Test.*—It has been stated that a very delicate means of detecting HCy is based upon its action on filtering paper, soaked, first, in a three-per-cent. alcoholic solution of guaiacum resin, and then in a two-per-cent. solution of cupric sulphate, and exposed to the air. The presence of HCy causes the production of a blue colour. The paper may be either moistened with the suspected solution or exposed to its vapour.

Cyanides are known,—

1. By giving off the odour of hydrocyanic acid when heated with sulphuric acid.
2. By answering to all the tests for hydrocyanic acid above mentioned.
3. In using the silver test to a soluble cyanide, the reagent must be added in excess, as argentic cyanide is soluble in alkaline cyanides to form double cyanides of silver and the alkali used.

Excess of argentic nitrate, however, decomposes these compounds, and forms insoluble argentic cyanide. The previous addition of a *slight* excess of dilute nitric acid ensures the immediate separation of the argentic cyanide, by preventing the reaction just referred to.

4. Insoluble cyanides yield cyanogen when heated *per se* in a small dry test tube, the open end of which has been drawn out into a jet after the introduction of the cyanide. The application of a light to the jet causes the characteristic flame of cyanogen.

38. SEPARATION OF CYANIDES FROM CHLORIDES.

Acidulate slightly with nitric acid, add *excess* of argentic nitrate, wash the precipitate thoroughly with boiling water by decantation, allow it to settle completely, pour off all the water, and boil with strong nitric acid, when the argentic cyanide dissolves, leaving the chloride insoluble. The solution in nitric acid is diluted and hydrochloric acid added, when any dissolved silver is detected by precipitation, as chloride.

39. CYANIC ACID and CYANATES, CYANURIC ACID, and FULMINIC ACID.

Cyanic acid is characterized,—

1. By being a colourless liquid, having a strong pungent odour, greatly resembling acetic acid, or sulphurous acid when in small quantity, and forming ammonium bicarbonate on adding water.
2. By changing into a white solid *isomer* on keeping, heat being evolved, but no decomposition occurring.

Cyanates are known,—

1. By giving, when moistened, a bicarbonate. (The potassium salt—KCyO—for instance, forms potassium bicarbonate—$KHCO_3$.)
2. By producing urea when evaporated with an ammonium salt.

Cyanuric acid is a polymeric modification of cyanic acid, which is recognised,—

1. By being a crystalline solid, yielding cyanic acid on applying heat.
2. By not being decomposed by strong hot HNO_3 or H_2SO_4.

Fulminic acid (intermediate between the two above acids) differs from both By the fearful explosibility of its salts.

40. THIOCYANIC ACID and THIOCYANATES (Sulphocyanates).

Sulphocyanic acid is known,

By being a colourless very acid liquid, which is not poisonous.

Sulphocyanates are recognised,

1. By being usually colourless and soluble, and evolving hydrocyanic acid and depositing sulphur on heating with sulphuric acid.
2. By producing with a ferric salt, a blood-red solution of *ferric sulphocyanate*—$Fe_2 6CyS$—the colour of which is not destroyed by HCl, but disappears on adding mercuric chloride—$HgCl_2$.

41. FERROCYANIC ACID and FERROCYANIDES.

Ferrocyanic acid (or hydroferrocyanic acid) is recognised,—

By being colourless at first, but rapidly decomposing and depositing Prussian blue.

Ferrocyanides are mostly insoluble in water, except those of the metals of the first and second groups. They are characterized,—

1. By giving off hydrocyanic acid and forming a deposit on heating with sulphuric acid.
2. By giving with a **ferrous salt** a white precipitate of ferrous potassium ferrocyanide—$K_2Fe(FeCy_6)$—changing quickly to blue.
3. By yielding with a **ferric salt** a dark blue precipitate of *ferric ferrocyanide*—$(Fe_2)_2 3(FeCy_6)$. This precipitate and (1) are both insoluble in HCl, but KHO decomposes them, producing potassium ferrocyanide. When it is boiled with HgO and water, mercuric cyanide—HgCy—and Fe_2O_3 remain.
4. **Cupric salts** produce a reddish-brown precipitate of cupric ferrocyanide—Cu_2FeCy_6—insoluble in acids, dissolved by NH_4HO, but left unaltered on evaporating off the ammonia.
5. By precipitating a white ferrocyanide from a solution of a lead salt.
6. By yielding a white mercuric ferrocyanide in a mercuric solution.
7. By giving no effect with magnesium salts but a white gelatinous precipitate, soluble in NH_4HO on the addition of a solution containing a zinc salt.
8. By producing with argentic nitrate—$AgNO_3$—white gelatinous silver ferrocyanide, dissolved by NH_4HO.

None of these precipitates can be produced in alkaline solutions; and they form best in neutral, or slightly acid, solutions.

42. FERRICYANIC ACID and FERRICYANIDES.

Ferricyanides are based upon *hydroferricyanic acid* (or ferricyanic acid)—$H_6Fe_2Cy_{12}$—which is characterized,—

By being a reddish-brown liquid decomposed by boiling, with evolution of HCy.

Most ferricyanides are insoluble, those of the alkalies and of the barium group being exceptions. They are recognised,—

1. By yielding an odour of hydrocyanic acid, and a deposit on heating with sulphuric acid.
2. By producing with a **ferrous** salt dark-tinted *Turnbull's blue*—$Fe_3Fe_2Cy_{12}$—insoluble in acids, but forming $K_6Fe_2Cy_{12}$ when boiled with KHO.
3. By producing a brownish coloration when added to a **ferric** salt in solution, from which H_2SO_3, *Stannous Chloride*—$SnCl_2$—and other reducing agents throw down *Turnbull's blue* or *Prussian blue* (*distinction between* $H_6Fe_2Cy_{12}$ *and* H_4FeCy_6).
4. By giving no precipitate in a lead solution (*another distinction of a ferricyanide from a ferrocyanide*).
5. By throwing down *mercurous ferricyanide* of a brownish-red colour from a mercurous solution.
6. By yielding with argentic nitrate solution an *orange* precipitate of argentic ferricyanide.
7. Mercuric salts, giving no precipitate.
8. Stannous salts, a white precipitate, soluble in HCl.
9. Stannic salts, no visible alteration.

43. SEPARATION OF FERRO- FROM FERRI- CYANIDES.

Acidulate with hydrochloric acid, add excess of ferric chloride, warm tly; the ferro-cyanide will be precipitated. Pour off some of the brownish

liquid and heat with a little zinc amalgam, when a blue precipitate will form, owing to the reduction of the ferri- to ferro- cyanide.

44. DETECTION OF CYANIDES IN THE PRESENCE OF FERRO- AND FERRI- CYANIDES.

Acidulate slightly with nitric acid and add an excess of a mixture of ferrous and ferric sulphates, warm gently, and allow the precipitate to subside. Pour off a little of the supernatant liquid, add to it excess of potassium hydrate and then acidulate with hydrochloric acid, when the production of another blue precipitate will prove the cyanide.

45. PHOSPHORUS and PHOSPHIDES.

The non-metal *phosphorus* has two varieties, characterized and distinguished as follows :—

A. *Ordinary phosphorus.* This is a yellowish wax-like solid, inflammable in a warm room, when exposed to the air in a dry state. Soluble in ether.

B. *Red, or amorphous phosphorus.* This is a dark reddish-brown solid, not readily inflammable. Not giving off vapours when exposed to the air, nor soluble in ether and CS_2

Phosphides are of little importance. They have usually the odour of phosphorus, and give off spontaneously inflammable phosphuretted hydrogen with water or dilute acid.

46. HYPOPHOSPHOROUS ACID and HYPOPHOSPHITES.

Hypophosphites are based upon the hydrogen salt, which is a colourless liquid, oxidized in the air. The silver salt alone is insoluble in water, and few are insoluble in alcohol.

The following reactions serve for their detection :—

1. When heated in a solid state, they take fire, evolving phosphuretted hydrogen, and leaving a residue of pyrophosphate.
2. With argentic nitrate they give a white precipitate, which turns brown owing to its reduction to metallic silver.
3. With mercuric chloride they yield, when slightly acidulated with HCl, a precipitate of calomel, which, on heating, turns dark, owing to a reduction to the metallic state.
4. Treated with zinc and sulphuric acid (nascent hydrogen) they yield phosphuretted hydrogen.
5. After removal of the base, the free hypophosphorous acid, when boiled with solution of cupric sulphate, will give a deposit of metallic copper.
6. Treated with ammonium molybdate they give a fine *blue* precipitate. As afterwards mentioned, *phosphates* give a *yellow*, and consequently when the solution contains both classes of salts the precipitate is *green*. This forms an excellent and rapid method of checking any commercial sample of hypophosphites.

They are distinguished from phosphites by not giving precipitates with neutral barium, or calcium, chloride, or with plumbic acetate. The 4th reaction above given is equally applicable to phosphites In performing the 5th reaction, the base, if calcium, is removed by oxalic acid, if barium, by sulphuric acid, and if a heavy metal, by sulphuretted hydrogen.

47. PHOSPHOROUS ACID and PHOSPHITES.

Phosphites are formed from *phosphorous acid*, which is the only comparatively stable liquid possessing the power of evolving *hydrogen phosphide*—PH_3—on being heated. The salts are distinguished as follows :—

1. Heated on platinum foil, they burn. They are powerful reducing agents.
2. The only phosphites soluble in water are those of K, Na, and NH_4, but acetic acid dissolves all, except plumbic phosphite.
3. With zinc and sulphuric acid (nascent hydrogen) they yield phosphuretted hydrogen, burning with an emerald-green colour, and throwing down Ag_3P, as well as Ag from $AgNO_3$ in solution.
4. They give precipitates with neutral barium, and calcium, chlorides, and also with plumbic acetate, which hypophosphites do not.
5. Heated with mercuric chloride or argentic nitrate, they yield a precipitate of metallic mercury or silver.

$$2\,HgCl_2 + 2H_3PO_3 + 2H_2O = 2H_3PO_4 + Hg_2 + 4HCl.$$

48. META- AND PYRO- PHOSPHORIC ACIDS AND THEIR SALTS.

As already stated in Part I., phosphoric anhydride can combine with water in three proportions, forming either meta-, pyro-, or ortho- phosphoric acids, each of which can form salts.

Metaphosphoric Acid is a glassy solid, not volatile by heat. It is freely soluble in cold water, and is converted by boiling into orthophosphoric acid. It is known by giving a white precipitate with argent-ammonium nitrate, and by its power of coagulating albumen. **Metaphosphates** are known by,—

1. Giving no precipitate with ammonium chloride, ammonium hydrate, and magnesium sulphate, added successively.
2. By giving a white precipitate of argentic metaphosphate—$AgPO_3$—with argentic nitrate only in neutral solutions, and soluble both in nitric acid and ammonium hydrate.

Pyrophosphoric Acid is also soluble in water and convertible by boiling into orthophosphoric acid. It gives a white precipitate with argent-ammonium nitrate, but does not coagulate albumen. Pyrophosphates are insoluble in water, except those of the alkalies. Their tests are not very well defined, but they give,—

1. A white precipitate of argentic pyrophosphate—$Ag_4P_2O_7$—with argentic nitrate in a neutral solution only and soluble both in nitric acid and ammonium hydrate.
2. NH_4MoO_4 does not produce an immediate precipitate.

49. ORTHOPHOSPHORIC ACID (B.P.) and ORTHOPHOSPHATES.

B.P. Phosphoric acid is a liquid with a strongly acid reaction, which is converted by heat first into pyro- and finally into meta- phosphoric acid, which remains as a glassy residue. It is,—

1. Not volatile by a red heat.
2. It gives a yellow precipitate of argentic phosphate—Ag_3PO_4—when treated with argent-ammonium nitrate, soluble both in nitric acid and ammonium hydrate.

Phosphates are as a rule insoluble in water, except the alkaline ones. They are readily soluble in dilute acids and entirely re-precipitated on neutralizing by an alkali or alkaline carbonate. Calcium, strontium, and barium

phosphates are only partly soluble in dilute sulphuric acid, being converted into a soluble phosphate and an insoluble sulphate of the metal. If the insoluble sulphate be filtered out, the addition of an alkali causes only a slight precipitate of a dimetallic phosphate, and a phosphate of the alkali used is left in solution; but it is only after the use of sulphuric acid that any phosphate thus remains dissolved.

The presence of Phosphates is detected as follows:—

1. With **barium** or **calcium chloride white precipitates** are produced, soluble in acetic acid (distinction from oxalates) and all stronger acids.
2. With **argentic nitrate** a **lemon yellow precipitate** of argentic phosphate forms, soluble both in nitric acid and ammonium hydrate.
3. With **ferric chloride** in the presence of **ammonium acetate** a white precipitate of **ferric phosphate** appears, insoluble in acetic acid.
4. With **magnesia mixture** phosphates yield a white crystalline precipitate, forming slowly in dilute solutions, consisting of **ammonium-magnesium phosphate**—$Mg(NH_4)PO_4 + 6H_2O$—soluble in acetic and all acids.
5. With solution of **ammonium molybdate** in **nitric acid** a yellow precipitate is produced, insoluble in nitric acid, but soluble in **ammonium hydrate.**
6. With **uranic nitrate** phosphates yield a yellow precipitate of *uranic phosphate*, also insoluble in acetic acid
7. With **mercurous** and **bismuthous nitrates** white precipitates are formed, the former soluble and the latter insoluble in nitric acid.
8. With any **soluble salt of lead** a **white precipitate** of **plumbic phosphate** is produced, soluble in nitric acid, but insoluble in acetic acid or ammonium hydrate.

It is important to note that all these reactions may be caused by **arsenic acid,** except that with argentic nitrate, argentic arseniate differing from argentic phosphate in being brick red instead of yellow.

50. DETECTION OF A PHOSPHATE IN THE PRESENCE OF CALCIUM, BARIUM, STRONTIUM, MANGANESE, AND MAGNESIUM.

Dissolve in water by the aid of the smallest quantity of nitric acid, then add excess of ammonium acetate, which will remove the excess of nitric acid without rendering the solution alkaline In this solution the phosphate may be proved by adding a drop or two of ferric chloride and warming, when a white precipitate of ferric phosphate—$Fe_2 2PO_4$—will form, insoluble in the acetic acid liberated.

51. DETECTION OF A PHOSPHATE IN THE PRESENCE OF IRON, CHROMIUM, AND ALUMINIUM.

Dissolve in the smallest possible quantity of hydrochloric acid, add some citric acid, and then excess of ammonium hydrate. By this means an alkaline liquid is obtained, owing to the power of the organic acid to prevent the precipitation of the metal by the ammonium hydrate, and in this liquid, when cold, *magnesia mixture* (ammonio sulphate of magnesia) causes the precipitation of white crystalline magnesium ammonium phosphate.

52. DETECTION OF Fe, Ce, Cr, Al, Mn, Ca, Sr, Ba, and Mg IN THE PRESENCE OF PHOSPHORIC ACID (SEPARATION OF METALS OF THE 3rd AND 4th GROUPS WHEN PRECIPITATED AS PHOSPHATES).

The separation of the insoluble phosphates of the metals of the 3rd and 4th groups is a very important point, as, in the case of the presence of phosphoric acid, the entire *modus operandi* already given under the separations of the metals, is useless. To determine the presence or absence of this complication the solution, after removal of the metals of the 1st and 2nd groups by HCl and H_2S, is evaporated to dryness and the residue heated to destroy oxalates and other organic matters. The residue is then dissolved in hydrochloric acid, diluted, and boiled with a few drops of nitric acid to raise any iron to the ferric state. A small portion of this prepared solution is then mixed with excess of nitric acid and ammonium molybdate—NH_4MoO_4 and warmed for some time, when the production of a yellow precipitate of ammonium phospho-molybdate proves the presence of phosphates. When this has been discovered, the remainder of the solution is treated with ammonium chloride and ammonium hydrate, as already explained under the metals, the group precipitate is filtered out and dissolved in the smallest possible quantity of hydrochloric acid. To this solution is added first a quantity of disodium hydrogen phosphate, and then an excess of ammonium acetate containing some free acetic acid, and the whole is boiled and filtered. By this means the phosphates are divided into two groups as follows:—

A. Insoluble in acetic acid, and consequently on the filter—Fe, Ce, Al, and a little Cr.

B. Soluble in acetic acid, and consequently remaining in the filtrate,—Ba, Sr, Ca, Mn, Mg, and the bulk of the Cr.

These groups are then to be treated as follows:—

A. Percolate the precipitate with a little boiling dilute solution of potassium hydrate; when any **aluminium** phosphate will dissolve, and be found in the filtrate by boiling with a slight excess of acetic acid. The insoluble matter on the filter is dissolved in dilute hydrochloric acid, and a portion of the solution tested for **iron** by potassium ferrocyanide. To the remainder of the solution add some citric acid, then excess of ammonium hydrate, and finally ammonium oxalate, when the production of a white precipitate of cerous oxalate proves **cerium**.

B. The solution, if green, contains **chromium**, and a little of it evaporated to dryness with excess of potassium hydrate and a crystal of potassium chlorate, and the residue heated to redness, becomes green, if **manganese** be present. (See 53.) Add to the remainder of the solution potassium chromate in slight excess, and warm, when any **barium** separates as barium chromate. Filter, if necessary, and add a few drops of very dilute sulphuric acid; warm, and let it stand for some time, when **strontium** will precipitate as strontium sulphate, insoluble on filtering out and boiling with strong solution of ammonium sulphate containing a slight excess of ammonium hydrate. Add to the filtrate some more ammonium acetate, and then excess of ammonium oxalate, and warm, when **calcium** will separate as calcium oxalate. Filter if necessary, cool thoroughly, and add some citric acid and excess of ammonium hydrate, when any manganous or magnesium phosphate will be re-precipitated. If no manganese was previously found by the fusion, then this is all **magnesium**; but if manganese be present, the following separation must be applied to the precipitate after filtering. The addition of citric acid is unnecessary if no chromium be present.

53. SEPARATION OF MANGANESE AND MAGNESIUM PHOSPHATES.

Dissolve in HCl, add excess of ammonium acetate, boil, and drop in ferric chloride until the precipitate turns red, then filter. This removes the phosphoric acid, and leaves the Mn and Mg in solution as chlorides. To this solution add NH_4Cl, NH_4HO, and NH_4HS, and warm, when the **manganese** will precipitate. Filter, cool the filtrate thoroughly, and add some more ammonium hydrate and some disodium hydrogen phosphate, when the **magnesium** will separate as a white precipitate of magnesium ammonium phosphate.

54. DETECTION OF CHROMIUM IN THE PRESENCE OF MANGANESE AFTER FUSION.

The deep green of the potassium manganate produced by the fusion, entirely masks any yellow potassium chromate which may be formed at the same time. On treating the manganese residue with water, it gives a *green solution*, which is *entirely decolorized* by boiling with hydrochloric acid and dropping in rectified spirit. On the other hand a chromium residue gives a *yellow solution*, turned *green* by a similar treatment. If, therefore, on thus boiling with acid and spirit, any green colour remains undischarged, then chromium was present as well as manganese.

55. ARSENIOUS ACID and ARSENITES.

Arsenious Acid—H_3AsO_3—is not known in the free state; but its anhydride —As_2O_3—is common. The latter has the following qualities:—

1. Dropped upon red hot charcoal or coal, or heated in a dry tube with black flux, or a mixture of dry sodium carbonate and potassium cyanide, the metalloid **As** is set free, and volatilizes with a garlic odour, producing a steel grey mirror on the sides of the tube.
2. Dissolved in water only, and argent-ammonium nitrate added, a canary-yellow precipitate of argentic arsenite—Ag_3AsO_3—is produced, soluble in excess of either NH_4HO or HNO_3.
3. A pure aqueous solution, mixed with cupr-ammonium sulphate, gives a bright green cupric arsenite—*Scheele's green*—also soluble in NH_4HO or in HNO_3.
4. Any solution yields all the tests for **arsenic** (see page 33).

Arsenites behave peculiarly in many respects. Ammonium arsenite leaves arsenious acid on evaporating a solution, while potassium and sodium arsenites possess a degree of alkalinity which no excess of arsenious acid will disturb. Ba, Sr, and Ca form soluble hydrogen salts. All other arsenites are insoluble.

Neutral solutions of **arsenites** are possessed of the undermentioned distinctive peculiarities:—

1. $CuSO_4$ throws down greenish cupric arsenite.
2. $AgNO_3$ is transformed into yellow insoluble argentic arsenite.
3. H_2S does not form a precipitate, except in the presence of hydrochloric acid, when yellow arsenious sulphide falls.
4. The solution gives the usual tests for **arsenic** (see page 33).

56. ARSENIC ACID and ARSENIATES.

Arsenic Acid—H_3AsO_4—is known definitely, but its *anhydride*—As_2O_5—is also of some importance, and should be first considered. It is recognised,—

By being a white crystalline solid, totally volatilized at a very bright red heat, owing to splitting up into As_2O_3 and oxygen.

The acid is known by the following characters :—

1. The crystals are deliquescent, white, and strongly acid. Before being dried at 212° F., they contain water of crystallization.
2. If heated to 300° F., they produce pyro-arsenic acid—$H_4As_2O_7$—which develops heat on being dissolved in water. More strongly heated (403° F.) *metarsenic acid*—$HAsO_3$—results, and finally As_2O_5.
3. It is strongly corrosive, and blisters the skin. It gives *brick-red* Ag_3AsO_4 on adding *argent ammonium nitrate.*

Arseniates are characterized by behaving in every respect exactly like phosphates, except that they give a brick-red precipitate with argentic nitrate, instead of a yellow. Insoluble arseniates are best treated by boiling with NaHO, filtering, *exactly neutralizing* the filtrate with dilute HNO_3, and then getting the brick-red precipitate with $AgNO_3$.

57. SEPARATION OF AN ARSENIATE FROM A PHOSPHATE.

This can only be done by acidulating with hydrochloric acid, and diligently passing a slow stream of sulphuretted hydrogen through the solution, kept warm until the whole of the arsenic is removed.

58. MANGANIC ACID and MANGANATES.

Manganic Acid—H_2MnO_4—is not known in the free state, neither is its *Anhydride*—MnO_3—but the salts are well known.

Manganates are unstable compounds, and only the alkaline salts dissolve in water, forming green solutions.

1. Soluble manganates decompose spontaneously, depositing MnO_2 (or $MnO2HO$), the green colour changing to purple or reddish violet, owing to the formation of a permanganate.

$$3K_2MnO_4 + 3H_2O = K_2Mn_2O_8 + 4KHO + MnO2HO.$$

2. Dilute acids effect this change more rapidly, and the reaction is very delicate. The free hydrate is then replaced by a chloride, nitrate, or sulphate.
3. Strong, heated H_2SO_4 acts as represented in this equation :—

$$K_2MnO_4 + 2H_2SO_4 = K_2SO_4 + MnSO_4 + 2H_2O + O_2.$$

4. Strong HCl causes the evolution of Cl. The other actions are similar to those of permanganates, but less energetic.

59. PERMANGANIC ACID and PERMANGANATES.

Permanganic Acid appears to be a violet liquid, volatilized in fumes of the same colour by heat, and condensing to a dark-brown sublimate. It decomposes below 100° F., evolving oxygen, and is stated to be a powerful bleaching agent. It attracts moisture strongly, and detonates when quickly heated. The salts (**permangantes**) behave as follows :—

Permanganates are known,—

1. By the magnificent violet colour of their solutions, which is entirely bleached by oxalic acid or by heating with hydrochloric acid and dropping in rectified spirit.
2. By giving off oxygen on heating and leaving a green residue.

3. By giving off oxygen when heated with sulphuric acid, often with explosive violence.
4. By evolving chlorine when simply mixed with hydrochloric acid.

60. CHROMIC ACID and CHROMATES.

Chromic Acid—H_2CrO_4—not being definitely proved to exist, is represented by its *anhydride*—CrO_3. This is a dark-red crystalline solid, and when mixed with an aqueous solution of *hydrogen* peroxide—H_2O_2—a *deep blue* liquid results, which is believed to contain *perchromic acid*—$HCrO_4$ or $H_2Cr_2O_8$. The liquid decomposes rapidly, unless ether be added, which lengthens its existence.

This test, for either CrO_3 or H_2O_2 is exceedingly delicate, the ethereal solution of perchromic acid separating from the water and thus concentrating the colour into a small bulk of ether.

Chromates of the alkalies are soluble, while those of the other metals are chiefly insoluble, but have very brilliant colours. They are very poisonous, and are detected as follows :—

1. **Soluble chromates** give a yellow precipitate with plumbic acetate or barium chloride, soluble in nitric acid, insoluble in acetic acid. The lead salt is darkened in colour by alkalies, and dissolves by free excess of hot KHO.
2. With argentic nitrate a dark-red precipitate, also soluble in nitric acid, and in NH_4HO, but not in acetic acid—$HC_2H_3O_2$.
3. Boiled with hydrochloric acid and alcohol, or any reducing agent, (for instance, sulphurous acid—H_2SO_3) they turn green, owing to the production of chromic chloride (or sulphate).
4. Treated with sulphuretted hydrogen, in the presence of hydrochloric acid, they turn green, and a deposit of sulphur takes place :—

$$2K_2Cr_2O_7 + 16HCl + 6H_2S = 2Cr_2Cl_6 + 4KCl + 3S_2 + 14H_2O.$$

5. Chromates, when treated with an acid, turn orange; and dichromates, when treated with potassium hydrate or any alkali, turn yellow. In this way they are mutually distinguished.
6. Heated with strong H_2SO_4 they give off oxygen.
7. Treated with an excess of sulphuric acid, and shaken up with ozonized ether (solution of hydric peroxide in ether), they give a gorgeous blue with the most minute traces.

61. STANNIC ACID and STANNATES (Stannites ?).

This is an unimportant compound, and is thrown down by an alkaline hydrate from a stannic salt. It is sometimes stated to be endowed with the composition Sn4HO, and at others, SnO2HO(H_2SnO_3).

Stannates are formed by the solution of the acid in an alkaline hydrate, and are detected in the examination for metals.

Stannites are said to be formed by the solution of stannous hydrates in an alkaline hydrate. They decompose on boiling with KHO, forming *stannates* and throwing down metallic tin.

$$2Sn2HO + 2KHO = K_2SnO_3 + Sn + 3H_2O.$$

62. ANTIMONIC ACID.

This is the white precipitate having the composition $HSbO_3$ formed on adding strong HCl to *potassium antimoniate;* and it is detected in the examination for metals.

63. FORMIC ACID and FORMATES.

Formic acid—$HCHO_2$—is the "organic" acid which contains the highest percentage of oxygen and approaches most nearly in composition to the supposititious carbonic acid—H_2CO_3. It is a tolerably stable liquid, boiling at the same temperature as water. Formates are all soluble in water; under the influence of heat and reagents formic acid behaves as follows:—

1. Distils without blackening or decomposition, the vapour being very acid.
2. Heated with H_2SO_4 it evolves CO, which, being free from CO_2, gives no effect when passed through *lime-water*, but burns with the usual pale blue flame.
3. It is distinguished from other acids derived from carbon (except carbonic and oxalic), by not undergoing charring, when mixed with sulphuric acid and heated. The reaction is:—

$$H_2SO_4 + HCHO_2 = H_2SO_4 + CO + H_2O.$$

4. It readily reduces argentic nitrate, when mixed with a little solution of sodium hydrate, and heat applied, metallic silver separating. *It does not* reduce platinic and auric chlorides when boiled with them, *unless sodium or potassium hydrate be added.* This is owing to the volatility of the acid.

64. DETECTION OF A FORMATE IN THE PRESENCE OF FIXED ORGANIC ACIDS WHICH REDUCE SILVER SALTS.

Distil with dilute sulphuric acid at the heat of a water bath, neutralize the distillate with sodium carbonate, add a *slight* excess of acetic acid, and boil with argentic nitrate, when a dark deposit of metallic silver will form.

65. ACETIC ACID and ACETATES.

This acid is characterized by its boiling point, its odour of vinegar, and the difficulty with which it is oxidized. The strong acid chars when heated with strong H_2SO_4.

Acetates are without exception soluble in water ($AgC_2H_3O_2$ and $HgC_2H_3O_2$ are sparingly dissolved). They are decomposed by a red heat, yielding *acetone* if the heat rise gently and the mass be not alkaline, and leaving a carbonate, oxide, or metal, according to the nature of the basylous radical. When heated with alkalies *marsh-gas*—CH_4—is evolved. The reaction is of this type:—

$$NaC_2H_3O_2 + NaHO = Na_2CO_3 + CH_4.$$

In the case of no hydrate or carbonate being present, the following is an example of the effect of heat on acetates:—

$$Ba2(C_2H_3O_2) = BaCO_3 + C_3H_6O_3 \quad \text{(Acetone).}$$

Acetates of easily reducible metals, such as copper, yield, when heated, a distillate of acetic acid, leaving a residue of the metal, or, in some cases, of oxide. The presence of **acetates** is analytically determined as follows:—

1. By evolving an odour of acetic acid when heated with sulphuric acid.
2. By a characteristic apple-like odour of "acetic ether,"—$C_2H_5(C_2H_3O_2)$—which they evolve when heated with sulphuric acid and rectified spirit.
3. By the deep red colour which they produce with neutral ferric

chloride,—ferric acetate $Fe_2(C_2H_3O_2)_6$—dischargeable by both hydrochloric acid and mercuric chloride.

4. Mercurous nitrate, when added to an acetate in strong solution, yields a crystalline white precipitate, which, on heating, leaves a residue of metallic mercury. This reaction is not, however, characteristic.

66. VALERIANIC ACID and VALERIANATES.

Valerianic acid is a liquid, which is :—

Volatile, malodorous, colourless, and oily. It reddens test-paper, and dissolves in most *menstrua*.

The general characters of **Valerianates** are :—

1. A more or less strong odour of valerian root when warmed or moistened.
2. They give, when heated with sulphuric acid, a distillate, which, on the addition of solution of cupric acetate, forms, after the lapse of some time, an oily precipitate ; gradually solidifying, by the absorption of water, into a greenish-blue crystalline solid.

67. SULPHOVINATES (Ethylsulphates).

These salts, derived from ethyl hydrogen sulphate, behave as follows :—

1. Heated with strong sulphuric acid, they evolve a faint ethereal odour.
2. They give no precipitate in the cold with barium chloride ; but on boiling, a white precipitate of barium sulphate falls, and a smell of alcohol is perceived. The addition of a little solution of barium hydrate after the chloride and before boiling facilitates the reaction ; but in this case all metals precipitable by a fixed alkali must first, of course, be removed.
3. Heated to redness, they leave a sulphate of the metal.
4. Heated with sulphuric acid and an acetate, or with strong acetic acid, they evolve acetic ether with its characteristic apple odour.

68. STEARIC ACID and STEARATES.

This acid is usually so distinguished by its appearance and behaviour on being heated, that further tests are useless. The characters are :—

1. A white, odourless, fatty solid, melting by heat, and then exhibiting an acid reaction.
2. Giving, when dissolved in KHO and the solution as nearly neutralized as possible, a white insoluble precipitate of plumbic stearate —$Pb2(C_{18}H_{35}O_2)$—on the addition of plumbic acetate, which is insoluble in ether (distinction from plumbic oleate).

Stearates of the alkalies are alone soluble in water.

Any stearate heated with dilute HCl gives the free acid, which floats as an oily liquid, solidifying on cooling to a white mass. This test is applicable to the analysis of soap (*hard*, containing Na, or *soft*, in which K is present).

69. OLEIC ACID and OLEATES.

Oleic Acid is usually an oily liquid, but remains solid below 59° F. when crystallized from alcohol.

It has no reaction, taste, nor odour, does not dissolve in water, but is taken up by cold H_2SO_4 (with decomposition) and by ether.

Oleates of **K** and Na alone dissolve in water. Acid oleates are all liquid and soluble in cold absolute alcohol and ether.

1. They do not separate out from either of these solvents when a hot solution is cooled (*distinction from stearates and palmitates*).
2. *Plumbic oleate* is precipitable like plumbic stearate, but is separated and distinguished from it by dissolving in ether.

70. LACTIC ACID and LACTATES.

The pure strong acid resembles *glycerin* in appearance, liberates hydrogen on adding zinc, and distils with partial decomposition. It dissolves in ether. It gives pure CO when heated with sulphuric acid.

Lactates are not very soluble in water. They,—

1. Are insoluble in ether.
2. *Argentic Lactate*—$AgC_3H_5O_3$—when boiled gives a dark precipitate, which on subsidence leaves a *blue liquid*.
3. Strong solution of an alkaline lactate when boiled with $HgNO_3$, deposits *crimson* or *pink* mercurous lactate—$HgC_3H_5O_3$.

71. OXALIC ACID and OXALATES.

The acid is very common, and is recognised,—

1. By its colourless prismatic crystals, which are strongly acid, effloresce when exposed to dry air, and volatilize on heating with partial decomposition.
2. By the complete discharge it effects of the colour of a solution of potassium permanganate—$K_2Mn_2O_8$—acidulated with dilute H_2SO_4.
3. By reducing $AuCl_3$ with the precipitation of the metal.
4. By producing free H_2SO_4 when added to solution of $CuSO_4$. (This is one of the very rare instances in which SO_4 is replaced by another acid radical and H_2SO_4 liberated.)
5. By giving the reactions of an oxalate.

Oxalates of the alkalies are soluble, the others insoluble, in water. Insoluble oxalates dissolve in hydrochloric but not in acetic acid. They are known by—

1. Not charring when heated, but only turning faintly grey; followed by a sudden glow of incandescence, which runs through the mass.
2. Not charring when heated with sulphuric acid, but yielding CO and CO_2 with effervescence.
3. Not effervescing with cold dilute sulphuric acid; but at once liberating CO_2 with effervescence on the addition of a pinch of manganese peroxide.
4. With calcium chloride or barium chloride in a neutral or alkaline solution, they give a white precipitate of calcium or barium oxalate, *insoluble in acetic acid, but soluble in hydrochloric acid.*

(For separation of oxalates from tartrates, etc., see No. 76.)

72. SUCCINIC ACID and SUCCINATES.

This acid is a white crystalline solid. It is known,—

1. By not charring with strong hot sulphuric acid.
2. By subliming in a tube open at both ends, in silky needles, *without giving off an irritating vapour* (distinction from benzoic acid).

3. By burning, when heated on platinum, with a blue smokeless flame.

Succinates are recognised as follows :—

1. With ferric chloride, a brownish-red precipitate of *ferric succinate*—$Fe_23(C_4H_4O_4)$—is formed.
2. With hydrochloric, and sulphuric, acids, no precipitate is produced (*distinction from benzoates*). With *plumbic acetate*, a white precipitate of *plumbic succinate*, soluble in succinic acid, succinates, and plumbic acetate.
3. *Barium succinate* is soluble in hydrochloric acid, hence no effect results from the addition of succinic acid to barium chloride; but alcohol and ammonium hydrate give rise to a white precipitate (*another point of distinction from benzoates*).

73. MALIC ACID and MALATES.

Malic Acid—$H_2C_4H_4O_5$—is a colourless, crystalline, very deliquescent acid, freely soluble in water and alcohol. Acid **malates** are most stable. The characters are :—

1. Calcium chloride, added to a neutral solution of a malate, gives no precipitate. Alcohol, however, even if added in small quantity, throws down a white precipitate; and boiling aids the effect.
2. Strong H_2SO_4 gives no charring for some time (*a tartrate is carbonized in a few minutes*).
3. Amorphous *plumbic malate* fuses below 100° C. in water, but not in an air-bath.

74. TARTARIC ACID and TARTRATES.

Tartaric Acid—$H_2C_4H_4O_6$—is a strong acid, soluble in water and spirit.

1. It forms usually oblique rhombic prismatic crystals, of an acid taste.
2. It is decomposed by heat, giving off the odour of *burnt sugar*, and leaving carbon. A similar effect is produced by boiling with strong H_2SO_4, which blackens and carbonizes it in a few minutes.
3. With potassium acetate—$KC_2H_3O_2$—it produces a white crystalline precipitate of *potassium hydrogen tartrate*—$KHC_4H_4O_6$—in either an aqueous or an alcoholic solution, soluble in much water, but not in spirit. Stirring or violent shaking promotes the formation of the salt.

The same compound is produced on adding any potassium salt, provided the liquid contain free excess of tartaric acid only.

Tartrates of the alkalies are mostly soluble; but the others are insoluble. The hydrogen tartrates of K and (NH_4) are nearly insoluble. Tartrates are recognised by the following characters :—

1. Heated to dull redness they char rapidly and give off a smell of burnt sugar. The black residue contains the metal as carbonate if it be K, Na, Li, Ba, Sr, or K, but the tartrates of other metals usually leave the oxides, or more rarely (as in the case of $Ag_2C_4H_4O_6$) the metal.
2. Heated with strong sulphuric acid, they blacken rapidly, and give first a smell of burnt sugar, and afterwards evolve SO_2.
3. Neutral solutions (free from more than a trace of ammonium salts) give, on adding **calcium chloride**, a white precipitate of *calcium tartrate*, which, when freed from other salts by washing, dissolves readily in cold solution of potassium hydrate, but is again pre-

cipitated on boiling. The precipitate is soluble in NH_4Cl, but not in NH_4HO.

4. Mix a tartrate with **sodium carbonate**, and filter the slightly alkaline solution, so that the only metal present shall be sodium. If this clear solution, after *slight* acidification with acetic acid, be mixed with argentic nitrate, the whole, on heating nearly to boiling in a clean tube, deposits *a beautiful mirror of metallic silver* upon the test-tube employed.
5. A tartrate prevents the precipitation (more or less perfectly) of the salts of Pb, Bi, Cd, Cu, Pt, Fe_2, Mn, Ni, Co, Cr, and Zn, by an alkaline hydrate in excess, or a phosphate.

75. CITRIC ACID and CITRATES.

Citric Acid—$H_3C_6H_5O_7$—is soluble in water and alcohol, but insoluble in pure ether. It entirely burns away when heated to redness in the air; blackens slowly when heated with strong sulphuric acid; and when neutralized by ammonium hydrate, and the solution cooled, the solution gives no precipitate with calcium chloride until it has been boiled. Added to ferric, chromic, or aluminic salts in solution, it prevents their precipitation by ammonium hydrate.

Citrates exhibit the following characters:—

1. Heated alone, they char slowly, and evolve an odour of burnt sugar, but not so intense as that of a tartrate. At a dull red heat, the citrates of K, Na, Li, Ba, Sr, and Ca leave their carbonates; but those of most other metals leave the oxides. Argentic citrate leaves the metal.
2. Heated with strong sulphuric acid, they slowly blacken, and evolve a slight odour of burnt sugar.
3. Mixed in the cold with calcium chloride, in the presence of a slight excess of ammonium hydrate, they give no precipitate; but on boiling, calcium citrate—$Ca_3 2C_6H_5O_7$—separates as a white precipitate. If this precipitate be filtered hot, and washed with a little boiling water, it is found to be quite insoluble in cold solution of potassium hydrate, but readily soluble in neutral solution of cupric chloride.
4. Mixed with argentic nitrate and boiled, no mirror of metallic silver is produced.

76. SEPARATION OF OXALATES, TARTRATES, CITRATES, and MALATES.

If the solution be acid, neutralize it with sodium hydrate; but if neutral or alkaline, it is ready for use, and is treated as follows:—

A. Acidulate slightly but distinctly with acetic acid, bring the whole to the boil, and add a drop or two of calcium chloride; and if it produce a precipitate, add it till precipitation ceases. Keep the whole nearly boiling for a time, till the precipitate aggregates, and filter. The precipitate, after washing, should be quite insoluble in cold solution of potassium hydrate.

B. To the filtrate from (*A*) mixed with some more calcium chloride, ammonium hydrate is added in slight but distinct excess, and the whole thoroughly cooled. Calcium tartrate precipitates, and when it has settled clear, the liquid is poured off and preserved for (*C*). This precipitate, after washing, should

be entirely soluble in cold solution of potassium hydrate, and reprecipitable by boiling.

C. The liquid is slowly boiled for some time; and if a precipitate does not form readily, a little more $CaCl_2$ and NH_4HO added, and the boiling resumed. The precipitate, when it begins to subside well, is filtered out while still hot. It should be (after washing) quite insoluble in cold solution of potassium hydrate; but soluble in perfectly neutral solution of cupric chloride.

D. To the filtrate add alcohol, when calcium malate will separate; but this portion of the separation is not infallible, and the precipitate must be carefully examined to see that it really is malate.

77. MECONIC ACID and MECONATES.

Meconic Acid is a white powder, with a strongly acid reaction, soluble in water, alcohol, and ether.

Meconates communicate a red colour to ferric chloride solution. This colour is *not discharged by $HgCl_2$ nor by dilute HCl.* By this means it is distinguished from a *sulphocyanate* and an *acetate.*

78. CARBOLIC ACID (or Phenic Acid) and CARBOLATES (Phenates).

The qualities of this acid are very distinctive.

1. It is a colourless, crystalline solid, melting at 94° F., and not volatile at 212°, having the odour and taste of creasote, being very poisonous, and not reddening test-paper.
2. The crystals deliquesce readily, forming a liquid which does not mix freely with water, but incorporates readily with alcohol, ether, and glycerin.
3. Mixed with HCl and exposed to the air on a strip of deal, it becomes greenish blue.
4. It coagulates *albumen.* It does not rotate polarized light.
5. Saturated with ammonia gas (NH_3) and heated in a closed tube, *aniline* is formed.

$$C_6H_5HO + NH_3 = C_6H_5H_2N + H_2O$$

6. It resembles HCy in not decomposing carbonates.
7. NH_4HO and $CaOCl_2$ produce a blue liquid.
8. It unites directly with strong H_2SO_4 to form sulpho-phenic (or sulpho-carbolic) acid—$C_6H_5HSO_4$.

Carbolates give the following reactions:—

1. When heated alone, they evolve the odour of carbolic acid and decompose.
2. Heated with strong sulphuric acid, they also smell of carbolic acid.
3. **Ferric chloride** causes a reddish-violet colour.

Sulpho-Carbolates behave similarly, but also give the reactions of a sulphate with barium chloride.

79. BENZOIC ACID and BENZOATES.

Benzoic Acid is of characteristic appearance, being usually seen in light feathery, flexible, nearly colourless crystalline plates or needles, and containing a trace of an agreeable volatile oil.

1. It is only slightly soluble in water, but dissolves freely in S. V. R., and in solutions of soluble hydrates.
2. Heated in the air, it burns with a luminous smoky flame; and when made hot in a tube open at both ends, sublimes in needles giving off an *irritating vapour.*

Benzoates possess the following general qualities:—

1. Heated with sulphuric acid they evolve the odour of benzoic acid, and darken.
2. Ferric chloride, in a solution made *slightly* alkaline by ammonium hydrate, gives a reddish-white precipitate—ferric benzoate—$Fe_2 6(C_7H_5O_2)$—soluble in acids (*benzoic* included). If this precipitate be now filtered out and digested in ammonium hydrate, it is decomposed into a precipitate of ferric hydrate, and a solution of ammonium benzoate, which is separated by filtration and treated as in 3.
3. Strong hot solutions of benzoates yield crystals of *benzoic acid* when hydrochloric acid is added, and the solution allowed to cool.
4. When distilled with potassium dichromate and sulphuric acid, they do not yield a distillate smelling of oil of bitter almonds (absence of *cinnamic acid,* which would form benzoic aldehyd when treated thus).

80. CINNAMIC ACID and CINNAMATES.

This may be recognised by reaction 4 (*above*) and also,—

By giving the product of benzoic aldehyd—C_7H_6O—when heated with PbO_2.

Cinnamates yield a precipitate of,—

Yellow *ferric cinnamate* — $Fe_2 6(C_9H_7O_2)$ — with ferric chloride (benzoates give a *reddish precipitate*).

81. SALICYLIC ACID ($H_2C_7H_4O_3$).

This acid occurs in large prisms, when crystallized from a solution in alcohol in which it is readily soluble. It is freely dissolved by hot water, but not readily by cold, requiring 1,800 parts of the latter to completely dissolve it.

1. Its aqueous solution gives with Fe_2Cl_6 a *deep violet coloration.* The compounds with methyl, ethyl, etc., give this reaction, as well as the ordinary salts.
2. Its methyl salt, formed by warming a salicylate with sulphuric acid and wood spirit, has a very fragrant odour.

From most other solid bodies it may be separated by taking advantage of its exceptionally great solubility in ether. In the event of its presence in an organic liquid (such as milk) it or its salts may be procured in a pure condition by dialysis. The liquid is placed in a dialyser, and this floated on pure water. The salicylic acid or salicylate is found after some time to have entirely passed through the septum, and may be obtained by evaporating the aqueous solution and, when reduced in bulk, shaking with ether.

82. DETECTION OF CARBOLIC ACID IN THE PRESENCE OF SALICYLIC ACID.

Boil 10 grains in half an ounce of water, cool, decant the solution and add to it 1 minim of a saturated solution of $KHCO_3$, 1 minim of aniline, and 5 drops of solution of *chlorinated lime,* when, if carbolic acid be present, a deep blue is produced.

83. TANNIC, GALLIC, and PYROGALLIC ACID.

Tannic Acid is soluble in water and alcohol, and very soluble in glycerin. It is insoluble in pure dry ether, but dissolves readily in ether containing a little water.

Gallic Acid is slightly soluble in cold water, but readily in boiling, it is also freely soluble in glycerin, and slightly in alcohol and ether.

Pyrogallic Acid is very soluble in water, the solution rapidly absorbing oxygen from the air and becoming brown. It also dissolves in alcohol and ether.

DISTINCTION BETWEEN GALLIC, TANNIC, AND PYROGALLIC ACIDS.

Behaviour of the Acid with	Gallic.	Tannic.	Pyrogallic.
Ferrous Salts . .	A dark solution is formed, gradually depositing a precipitate.	The same effect as Gallic.	A blue solution.
Ferric Salts . .	Purplish precipitate immediately formed.	Same as preceding.	A red solution.
Calcium Hydrate in the form of *Milk of Lime.*	A brownish precipitate, becoming deep brown in a few seconds.	A white precipitate slowly changing.	Instantaneous production of a purple solution becoming brown by oxidation.
Gelatin	No precipitate (except in the presence of gum).	Immediate brownish precipitate.	No precipitate.

CHAPTER IV.

QUALITATIVE ANALYSIS, AS APPLIED TO THE EXAMINATION OF OFFICIAL SALTS.

NAME.	PROOF OF PRESENCE OF THE PROPER CONSTITUENTS.	PROOF OF FREEDOM FROM IMPURITIES.
	1. CHLORIDES.	
Acidum Hydrochloricum. Hydrochloric Acid.	A strongly acid liquid, which, when evaporated to dryness, leaves no residue. It yields a curdy white precipitate with argentic nitrate, which is soluble in excess of ammonium hydrate, but insoluble in nitric acid (presence of combined chlorine).	When diluted with four times its volume of distilled water it gives no precipitate with a solution of barium chloride (absence of sulphuric acid), nor with sulphuretted hydrogen (absence of metallic impurities), and does not tarnish or alter the colour of bright copper foil when boiled along with it (absence of arsenic). If a fluid drachm of hydrochloric acid be mixed with half an ounce of distilled water, and thereafter be poured into a small flask containing a few fragments of granulated zinc, and, while effervescence continues, a slip of bibulous paper wetted with a solution of plumbic subacetate be introduced into the upper portion of the flask for about the space of five minutes, it will not become discoloured (absence of sulphurous acid, which would be reduced to sulphuretted hydrogen by the nascent hydrogen from the zinc and acid, and black plumbic sulphide formed on the paper).
Ammonii Chloridum. Ammonium Chloride.	Soluble in water and in rectified spirit. Its aqueous solution, when heated with potassium hydrate, evolves ammonia gas (NH_3), and when treated with argentic nitrate forms a copious curdy precipitate (presence of chloride).	When heated it volatilizes without decomposition and leaves no residue (absence of iron and fixed matters generally).

Sodii Chloridum. Sodium Chloride.	Imparts a yellow colour to flame (presence of sodium); and is soluble in water. The solution gives, with argentic nitrate, a white, curdy precipitate, soluble in ammonium hydrate, but insoluble in nitric acid (presence of chloride).	The aqueous solution should give no precipitate with platinic chloride (absence of potassium).
Calcii Chloridum. Calcium Chloride.	The solution gives a white precipitate with ammonium oxalate, insoluble in acetic acid (presence of calcium), and also a curdy white with argentic nitrate (presence of chloride).	Evolves no chlorine or hypochlorous acid on the addition of hydrochloric acid (absence of hypochlorites); it is entirely soluble in twice its weight of water, also in alcohol (absence of calcium hydrate or carbonate). The aqueous solution is not precipitated by the addition of lime-water (absence of carbonic acid).
Zinci Chloridum. Zinc Chloride.	Ammonium hydrate throws down a white precipitate (zinc hydrate), entirely soluble in an excess of the reagent; and the subsequent addition of ammonium sulphide causes a white precipitate (presence of zinc). Argentic nitrate added to the original solution causes a curdy white precipitate (presence of chloride).	If first acidulated with hydrochloric acid, it is not affected by sulphuretted hydrogen (absence of lead). Its watery solution is not affected by barium chloride (absence of sulphate), nor ammonium oxalate (absence of calcium), and is not tinged blue by potassium ferrocyanide or potassium ferricyanide (absence of ferric and ferrous salts).
Hydrargyri Subchloridum. Mercurous Chloride.	Digested with potassium hydrate it becomes black (owing to formation of mercurous oxide—Hg_2O); and the clear solution acidulated with nitric acid gives a copious white precipitate with argentic nitrate (presence of chloride); contact with hydrocyanic acid also darkens its colour. It is entirely volatilized by a sufficient heat.	Warm ether which has been shaken with it in a bottle, leaves on evaporation no residue (absence of mercuric chloride).
Hydrargyri Chloridum. Mercuric Chloride.	Its aqueous solution gives a yellow precipitate with potassium hydrate (mercuric oxide), a white precipitate with ammonium hydrate (mercuric ammonium chloride and absence of calomel), and a curdy white precipitate with argentic nitrate (presence of chloride).	When heated, it sublimes without leaving any residue (absence of fixed impurities).

Name.	Proof of Presence of the Proper Constituents.	Proof of Freedom from Impurities.
	Chlorides (*continued*).	
Hydrargyrum Ammoniatum. Mercur-ammonium Chloride.	Digested with potassium hydrate it evolves ammonia gas (NH_3), acquiring a pale yellow colour; and the fluid filtered, and acidulated with nitric acid, gives a white precipitate with argentic nitrate (presence of chloride). Boiled with a solution of *stannous chloride* it becomes grey, and affords globules of metallic mercury.	Entirely volatilized at a heat under redness (absence of white-lead and chalk, etc.). Should not fuse before volatilizing (distinction from the old London white precipitate).
Liquor Ferri Perchloridi. Ferric Chloride.	Diluted with water it gives a deep blue precipitate with potassium ferrocyanide (presence of iron), but no blue with potassium ferricyanide (proof of ferric salt). It forms a white curdy precipitate with argentic nitrate, soluble, after washing, in ammonium hydrate (presence of chloride).	Gravimetric quantitative analysis (which see).
Platinic Chloride.	Heated to a high temperature it leaves metallic platinum. With strong solution of potassium chloride it yields a yellow precipitate. Argentic nitrate gives a yellowish-white precipitate (argentic chloro-platinate) which does not behave exactly like argentic chloride; and therefore the most definite proof of the presence of combined chlorine is to warm with sulphuric acid and manganic peroxide, a smell of chlorine being evolved.	The aqueous solution precipitated with excess of sulphuretted hydrogen, and the precipitate removed, should give no residue on evaporation (general fixed impurities).
Stannous Chloride.	Boiled with mercuric chloride it gives first a white and then a grey precipitate, and with auric chloride a purple precipitate (presence of tin). With argentic nitrate it gives a white curdy precipitate, soluble, after washing, in ammonium hydrate (presence of chloride).	Heated for some time with a drop or two of aniline it should not develop a red colour (absence of stannic chloride).

Antimonii Chloridum. Antimonious Chloride.	A little of it dropped into water gives a white precipitate (antimonious oxychloride), and the filtered solution lets fall a copious white precipitate on the addition of argentic nitrate (presence of chloride). If the white precipitate formed by water be treated with sulphuretted hydrogen, it becomes orange coloured (antimonious sulphide—Sb_2S_3).	The filtered solution from the antimonious oxychloride should give no blue precipitate with potassium ferrocyanide (absence of ferric chloride added to give a deep colour).
	2. HYPOCHLORITES.	
Soda Chlorata. Chlorinated Soda.	It has a feeble odour of chlorine, and decolorizes sulphate of indigo. It effervesces with hydrochloric acid, evolving chlorine (proof of hypochlorite) and carbonic anhydride, and forms a solution which gives a yellow flame (presence of sodium).	Platinic chloride to a solution acidulated with HCl gives no yellow precipitate (absence of potassium). The original solution gives no precipitate with ammonium oxalate (absence of calcium). Also strength by volumetric analysis (which see).
Calx Chlorata. Chlorinated Lime.	Possesses a feeble odour of chlorine, and is partially soluble in water. The solution evolves chlorine copiously upon the addition of oxalic acid (proof of hypochlorite), and deposits at the same time calcium oxalate (presence of calcium).	Amount of "*available chlorine*" by volumetric analysis (which see).
	3. CHLORATES.	
Potassæ Chloras. Potassium Chlorate.	Its solution is not affected by argentic nitrate, but a crystal or two heated evolves oxygen, and the residue dissolved in the least possible quantity of water and divided into two parts gives a yellow precipitate with platinic chloride (proof of potassium), and a curdy white with argentic nitrate (proof of chloride produced by ignition).	No precipitate with argentic chloride in the original solution indicates absence of chlorides. Ammonium oxalate should give no precipitate (absence of calcium).

NAME.	PROOF OF PRESENCE OF THE PROPER CONSTITUENTS.	PROOF OF FREEDOM FROM IMPURITIES.
	4. IODIDES.	
Iodum. Iodine.	When heated, yields a beautiful violet-coloured vapour; very sparingly soluble in water, but freely soluble in alcohol and ether and a solution of potassium iodide. The aqueous solution strikes a deep blue colour with starch (blue iodide of starch).	It sublimes without leaving any residue, and the portion that comes over does not include any slender colourless prisms, emitting a pungent odour (iodic cyanide—ICy).
Potassii Iodidum. Potassium Iodide.	Its solution mixed with mucilage of starch gives a blue colour on the addition of a minute quantity of solution of chlorine, the chlorine liberating the iodine, which combines with the starch, forming blue *iodide of starch.* It gives a crystalline precipitate with tartaric acid (presence of potassium).	The addition of tartaric acid and mucilage of starch to its watery solution does not develop a blue colour (absence of iodate); solution of argentic nitrate added in excess forms a yellowish-white precipitate (argentic iodide), which when agitated with ammonium hydrate yields by subsidence a clear liquid, in which excess of nitric acid causes no turbidity (absence of chlorides or bromides). Its aqueous solution is only faintly precipitated by the addition of saccharated solution of lime (absence of carbonates).
Cadmii Iodidum. Cadmium Iodide.	Heated it fuses and gives off violet vapours. The aqueous solution gives a yellow precipitate (cadmium sulphide) with sulphuretted hydrogen or ammonium sulphide, which is insoluble in excess of the latter; the solution also gives a white gelatinous precipitate with *excess* of potassium hydrate (distinction from zinc).	The excess of the ammonium sulphide filtered from the yellow precipitate should give no reaction for arsenic, and the excess of potassium hydrate after filtering from the white precipitate should not give any precipitate with potassium ferrocyanide after acidulation by acetic acid (absence of zinc).
Hydrargyri Iodidum Viride. Mercurous Iodide.	Gradually heated in a test-tube it yields a yellow sublimate, which upon friction after cooling becomes red, and white globules of metallic mercury are left at the bottom of the tube (decomposition into mercuric iodide and mercury).	Nothing dissolved when shaken in a tube with ether (absence of mercuric iodide).

Hydrargyri Iodidum Rubrum. Mercuric Iodide.	When heated on a piece of paper, it turns red. It is soluble in ether, and in solutions of mercuric chloride or potassium iodide (distinction from mercurous iodide). When digested with solution of sodium hydrate, it assumes a reddish-brown colour, and the fluid (solution of sodium iodide) cleared by filtration and mixed with solution of starch gives a blue precipitate on being acidulated with nitric acid (presence of iodide).	Entirely volatilized at a heat under redness (absence of fixed impurities, and of mercurous iodide, which leaves metallic mercury).
Ferri Iodidum. Ferrous Iodide.	Its solution gives a copious blue precipitate with potassium ferricyanide (presence of iron). Mixed with mucilage of starch, it acquires a blue colour on the addition of a minute quantity of solution of chlorine (presence of iodide).	Its solution should not be coloured yellowish, nor have any rusty insoluble deposit (absence of free iodine and ferric iodide).
Plumbi Iodidum. Plumbic Iodide.	Sufficiently soluble in warm water to prove the iodide with starch paste and nitric acid. Dissolve a portion in water by the aid of potassium hydrate, and add excess of ammonium sulphide, when a copious black precipitate of plumbic sulphide will fall. This may be washed well and dissolved in diluted nitric acid by the aid of heat, and the resulting solution tested for lead in the usual manner.	General tests.
	5. BROMIDES.	
Potassii [B]romidum. [Pot]assium [Bro]mide.	Its aqueous solution gives a white crystalline precipitate with tartaric acid (proof of potassium). When its solution in water is mixed with a little chlorine, chloroform agitated with it, on falling to the bottom, exhibits a reddish colour (presence of bromide).	Volumetric analysis (which see).

NAME.	PROOF OF PRESENCE OF THE PROPER CONSTITUENTS.	PROOF OF FREEDOM FROM IMPURITIES.
	BROMIDES (*continued*).	
Ammonii Bromidum. Ammonium Bromide.	A solution heated with potassium hydrate evolves the smell of ammonia. A drop or two of chlorine water added and the whole shaken up with chloroform, the latter on separating is coloured red (presence of bromide).	A solution of the salt in water mixed with mucilage of starch, and a drop of an aqueous solution of bromine or chlorine does not exhibit any blue colour (absence of iodine). Entirely volatile by heat (absence of fixed impurities).
	6. HYDRATES.	
Liquor Ammoniæ. Ammonium Hydrate.	Strong smell of NH_3. Is strongly alkaline, and yet when diluted with H_2O it does not effervesce with HCl.	When diluted with four times its volume of distilled water, it gives no precipitate with solution of calcium hydrate (absence of carbonic acid gas), ammonium oxalate (absence of calcium), ammonium sulphide (absence of iron), or cuprammonium sulphate (absence of arsenic). When treated with an excess of nitric acid it is not rendered turbid by argentic nitrate, nor by barium chloride (absence of chlorides and sulphates). Also volumetric analysis (which see).
Liquor Sodæ, or *Soda Caustica* (dissolved in water).	Gives a yellow flame (presence of sodium). Is strongly alkaline, does not effervesce with HCl, and gives a brownish-black with $AgNO_3$ (presence of soluble hydrate).	Mixed with an equal volume of water it gives no precipitate with solution of calcium hydrate (absence of carbonates). When treated with an excess of diluted nitric acid, and evaporated to dryness, the residue is entirely soluble (absence of silica), and forms with water a clear solution, which is only slightly precipitated by barium chloride (comparative absence of sulphates) or by argentic nitrate (comparative absence of chlorides), and not at all by ammonium hydrate (absence of aluminium) or by sulphuretted hydrogen (absence of lead). Also volumetric analvsis (which see).

Liquor Potassæ, or *Potassa Caustica* (dissolved in water).	Gives after acidulation with HCl a yellow precipitate with $PtCl_4$ (presence of potassium). Is strongly alkaline, does not effervesce with HCl and gives a brownish-black with $AgNO_3$ (presence of soluble hydrate).	It does not effervesce when added to an excess of diluted hydrochloric acid mixed with an equal volume of distilled water, gives no precipitate with solution of calcium hydrate (absence of carbonates), nor ammonium oxalate (absence of calcium). When treated with excess of dilute nitric acid, and evaporated to dryness, the residue is entirely soluble in H_2O (absence of silica), and forms with water a nearly clear solution, which may be slightly precipitated by barium chloride (presence of a trace only of sulphates), argentic nitrate (presence of a trace of chlorides), and by ammonium hydrate (traces of aluminium and iron), but not at all by sulphuretted hydrogen (absence of lead). Also volumetric analysis (which see).
Liquor Calcis, or *Calcis Hydras* (dissolved in water).	Gives with $(NH_4)_2C_2O_4$ a white precipitate (presence of calcium). Is alkaline, does not effervesce with HCl, and gives a brownish-black with $AgNO_3$ (presence of soluble hydrate).	Not important, being all insoluble in water, and consequently not extracted in making the *liquor.* Also volumetric analysis (which see).
Ferri Peroxidum Humidum. Ferric Hydrate.	Dissolves readily in diluted hydrochloric acid, without effervescence or the aid of heat; and the solution gives a copious blue precipitate with potassium ferrocyanide, but not with potassium ferricyanide (denoting that all the Fe is in the ferric state).	None of importance.
[illegible]i Peroxidum [illegible]tratum. [illegible]rric [illegible]drate.	It dissolves completely, though slowly, without the aid of heat in hydrochloric acid diluted with half its volume of water (Fe_2O_3 would require heat); and solution gives a precipitate with potassium ferrocyanide, but none with potassium ferricyanide	None of importance.

NAME.	PROOF OF PRESENCE OF THE PROPER CONSTITUENTS.	PROOF OF FREEDOM FROM IMPURITIES.
	HYDRATES (*continued*).	
	(showing Fe in the ferric state only). Heated to dull redness in a test-tube, it gives off moisture, and becomes transformed into ferric oxide (proof of water of hydration).	
	7. OXIDES.	
Argenti Oxidum. Silver Oxide.	At a low red heat it gives off oxygen, and is reduced to the metallic state. It dissolves completely in nitric acid, without the evolution of any gas (absence of metallic silver), forming a solution which gives a curdy white precipitate with HCl instantly soluble in NH_4HO (presence of silver).	The nitric acid solution evaporated after separation of the Ag by HCl and filtration, should leave no residue (general absence of other metals).
Calx. Calcium Oxide.	The powder obtained by the process of *slaking*, when agitated with distilled water, gives, after filtration, a clear solution which has an alkaline reaction, and yields a white precipitate with ammonium oxalate (presence of calcium).	The powder obtained by slaking dissolves, without much residue (comparative absence of silica), and without effervescence (absence of CO_2), in dilute hydrochloric acid, and if the solution thus formed be evaporated to dryness, and the residue re-dissolved in water, only a very scanty precipitate forms on addition of saccharated solution of lime (comparative absence of aluminic and ferric oxides).
Magnesia. Magnesium Oxide.	It dissolves without effervescence or smell in HCl, and the solution, when neutralized by a mixed solution of ammonium hydrate and ammonium chloride, gives a copious crystalline precipitate on the addition of sodium phosphate (forming ammonium magnesium phosphate (proving magnesium).	Dissolved in nitric acid and neutralized by a mixture of ammonium chloride and ammonium hydrate (to prevent precipitation of magnesium hydrate by the ammonium hydrate), it does not give any precipitate with ammonium oxalate (absence of calcium) or barium chloride (absence of sulphates).

Zinci Oxidum. Zinc Oxide.	Becomes pale yellow when heated, but resumes its original colour on cooling. Dissolves without effervescence in dilute nitric acid (absence of carbonate), forming a solution, a portion of which gives, with ammonium carbonate, a white precipitate, which dissolves entirely, without colour, in an excess of the reagent, forming a solution which is precipitated white with ammonium sulphide. Another portion gives a white precipitate with potassium ferrocyanide (proofs of zinc).	The nitric acid solution is not affected by barium chloride (absence of sulphates) nor argentic nitrate (absence of chlorides). The whiteness of the ferrocyanide precipitate indicates the absence of iron; and a portion of the oxide dissolved in HCl should give no colour with sulphuretted hydrogen (absence of lead).
Lotio Hydrargyri Nigra. Active principle Mercurous Oxide.	Contains a black sediment (Hg_2O) insoluble in HCl alone, but soluble on the addition of a crystal of $KClO_3$, and the solution gives a grey precipitate when boiled with $SnCl_2$ (proof of mercury).	The supernatant liquid should give no yellow precipitate with potassium hydrate (absence of dissolved Hg—*ic*).
Hydrargyri Oxidum Flavum and *Hydrargyri Oxidum Rubrum,* both Mercuric Oxide.	Readily dissolved by hydrochloric acid, yielding a solution which when potassium hydrate is added in excess, gives a yellow precipitate (mercuric oxide), and with solution of ammonium hydrate, a white precipitate (mercur-ammonium chloride). Entirely volatilized by heat under redness, being at the same time decomposed into mercury and oxygen. If this be done in a test-tube, no orange vapours are perceived (absence of nitrogen oxides).	(1) *Red lead,* which is detected by the formation of a precipitate of plumbic peroxide when the sample is dissolved in dilute nitric acid. (2) *Undecomposed basic mercuric nitrate,* detected by red fumes on heating. (3) *Brickdust* remains insoluble in dilute nitric acid, and is known by its appearance. (4) *Cinnabar* (native red mercuric sulphide) is left as a residue on dissolving the sample in dilute hydrochloric acid. (5) *Mercurous oxide* is also insoluble in hydrochloric acid, as well as calomel, which is sometimes, but rarely found.
Manganic Peroxide.	Dissolves in heated hydrochloric acid with evolution of chlorine (proving peroxide), and the solution gives, when neutralized by ammonium hydrate and ammonium sulphide, a flesh-coloured precipitate, which is	General quantitative analysis (which see).

Name.	Proof of Presence of the Proper Constituents.	Proof of Freedom from Impurities.
	Oxides (*continued*).	
	soluble in acetic acid (proof of manganese). Heated on platinum foil with potassium hydrate and chlorate, a green residue is formed (confirming Mn).	
Potassæ Permanganas. Potassium Permanganate.	A single small crystal suffices to form, with an ounce of water, a rich purple solution, which when mixed with a little rectified spirit, and heated, becomes yellowish-brown (reduction and deposition of manganic peroxide). The crystals, when heated to redness, decrepitate, evolve oxygen gas, and leave a black residue, from which water extracts potassium hydrate, recognised by its alkaline reaction, and by its giving, when acidulated with hydrochloric acid, a yellow precipitate with platinic chloride.	Quantitative analysis (which see).
Ferri Oxidum Magneticum. Ferroso-ferric Oxide.	It dissolves, without effervescence, in hydrochloric acid, diluted with half its volume of water (absence of carbonate, and forming ferrous and ferric chlorides). The solution thus obtained gives a blue precipitate, both with potassium ferrocyanide and with potassium ferricyanide (presence of iron both in the ferrous and ferric states). When a small quantity is heated in a test-tube by the flame of a lamp, a deposit of moisture takes place in the cool part of the tube (water of hydration).	Volumetric analysis (which see).
Plumbi Oxidum. Plumbic Oxide.	Dissolves in heated acetic acid without effervescence; and the solution gives with potassium chromate	General analysis.

	and potassium iodide yellow precipitates, and with sulphuric acid a white precipitate, turned black by sulphuretted hydrogen (proofs of lead).	
Red Lead. Lead Plumbate.	Heated strongly, it turns yellowish, but does not volatilize; warmed with dilute nitric acid, it partly dissolves, depositing a brown precipitate (PbO_2), and the solution gives the usual tests for Pb. Entirely soluble in strong acetic acid.	General analysis.
Brown Lead. Plumbic Peroxide.	Soluble in heated hydrochloric acid with evolution of chlorine; and the solution on cooling deposits a crystalline mass of $PbCl_2$, which dissolves on boiling in a large volume of water; and the solution gives while hot the tests for Pb.	General analysis.
Antimonii Oxidum. Antimonious Oxide.	Fusible at a low red heat, insoluble in water, but readily dissolved by hydrochloric acid. The solution, dropped into distilled water, gives a white deposit, at once changed to orange by sulphuretted hydrogen. It dissolves entirely when boiled with an excess of potassium acid tartrate.	The solubility in $KHC_4H_4O_6$ shows absence of the higher oxides of antimony.
Bismuthi Oxidum. Bismuthic Oxide.	Heated to incipient redness it is not diminished in weight. It is insoluble in water, but soluble in nitric acid mixed with half its volume of water; and if it be thus dissolved to saturation, the solution mixed with ten or twenty times its volume of water yields a white precipitate (bismuthyl nitrate).	The nitric acid solution gives no precipitate with diluted sulphuric acid, nor with solution of argentic nitrate dropped into it (respective absence of lead and chlorides). Solution of ammonium chloride added to the nitric acid solution gives a white precipitate, and if this be treated with excess of ammonium hydrate, then filtered, and the clear filtrate neutralized with hydrochloric acid, it will not become turbid (absence of silver).

Name.	Proof of Presence of the Proper Constituents.	Proof of Freedom from Impurities.
	Oxides (*continued*).	
PotassæBichromas Potassium Bichromate.	Fuses below redness; at a higher temperature is decomposed, yielding green oxide of chromium and yellow chromate of potash, which may be separated by dissolving the latter in water. This solution gives a yellowish-white precipitate with barium chloride, and a purplish-red precipitate with argentic nitrate (test for character); both precipitates are soluble in dilute nitric acid. Strong solution digested with sulphuric acid and rectified spirit, acquires a deep green colour, and the liquid when cold gives a green precipitate with ammonium hydrate (Cr) and a yellow with platinic chloride (K).	General analysis; but usually fairly pure in commerce.
	8. CARBONATES.	
LithiæCarbonas. Lithium Carbonate.	It dissolves with effervescence in hydrochloric acid (proof of carbonate); and the solution evaporated to dryness leaves a residue of lithium chloride, which communicates a red colour to the flame of a spirit lamp, and re-dissolved in water yields a precipitate with sodium phosphate (proof of lithium).	Quantitative analysis (which see).
Ammoniæ Carbonas. Ammonium Carbonate.	It volatilizes entirely when heated, and is readily dissolved by acids with effervescence; and the solution gives off NH_3 when boiled with excess of potassium hydrate.	If diluted nitric acid be added to it in slightexcess, and the solution be boiled, it will give no precipitate with chloride of barium or nitrate of silver. Also volumetric analysis (which see).

Sodæ Carbonas. Sodium Carbonate.	Effervesces with acids (proof of carbonate), gives a yellow flame (proof of sodium) and a brick-red precipitate with mercuric chloride (distinction from bicarbonate).	In diluted hydrochloric acid, it forms a solution which does not precipitate with platinic chloride (absence of potassium). By heat it undergoes aqueous fusion, and then dries up, losing 63 per cent. of its weight (proper amount of water of crystallization). When supersaturated with nitric acid, it precipitates only slightly with barium chloride or argentic nitrate (absence of all but traces of sulphates and chlorides). Also volumetric analysis (which see).
Sodæ Bicarbonas. Sodium Bicarbonate.	Effervesces strongly with acids (presence of carbonate), gives a yellow flame (proof of sodium), and does not precipitate mercuric chloride red (distinction from carbonate).	Dissolves with much effervescence in diluted hydrochloric acid, forming a solution in which platinic chloride causes no precipitate (absence of potassium). A solution of the salt in cold water gives a white and not a coloured precipitate with solution of mercuric chloride (absence of undecomposed carbonate). When supersaturated with nitric acid its solution scarcely precipitates with barium chloride or argentic nitrate (practical absence of sulphates and chlorides). Also volumetric analysis (which see).
Potassæ Carbonas. Potassium Carbonate.	Effervesces with diluted hydrochloric acid (proof of carbonate), and forms a solution with which platinic chloride gives a yellow precipitate (proof of potassium).	Loses about 16 per cent. of its weight when exposed to a red heat (allowable amount of absorbed water). When supersaturated with nitric acid, and evaporated to dryness, the residue is almost entirely soluble in water, only a little silica remaining undissolved; and the solution is precipitated only faintly by barium chloride and argentic nitrate (traces only of sulphates and chlorides). Also volumetric analysis (which see).
Potassæ *rbonas.* tassium rbonate.	Diluted hydrochloric acid causes strong effervescence (proof of carbonate), forming a solution with which platinic chloride gives a yellow precipitate (proof of potassium).	Volumetric analysis after ignition of 50 grains, which should leave $34\frac{1}{2}$ grains of K_2CO_3 (see volumetric analysis).

Name.	Proof of Presence of the Proper Constituents.	Proof of Freedom from Impurities.
	Carbonates (*continued*).	
Calcis Carbonas Precipitata. Precipitated Calcium Carbonate.	Dissolves with effervescence in diluted hydrochloric acid (proof of carbonate). This solution, when supersaturated with ammonium hydrate, gives, upon the addition of ammonium oxalate, a copious white precipitate (proof of calcium).	The salt formed by dissolving the prepared chalk in nitric acid, if rendered neutral by evaporation to dryness and re-dissolved in water, gives no precipitate either on the addition of saccharated solution of lime (absence of iron and alumina) or of argentic nitrate (absence of chlorides).
Magnesiæ Carbonas. Magnesium Hydrato-carbonate.	Dissolves with effervescence in the diluted mineral acids (proof of carbonate), yielding solutions which, when first treated with ammonium chloride, are not disturbed by the addition of an excess of ammonium hydrate, but yield a copious crystalline precipitate upon the addition of sodium phosphate (proof of magnesium).	With excess of hydrochloric acid it forms a clear solution in which chloride of barium causes no precipitate (absence of sulphate). Another portion of the solution supersaturated with ammonium hydrate gives no precipitate with oxalic acid (absence of calcium) or sulphuretted hydrogen (absence of iron and lead). Fifty grains calcined at a red heat are reduced to twenty-two (proper amount of carbonate). The fact that ammonium hydrate gives no precipitate when added to the acid solution, proves absence of alumina.
Zinci Carbonas. Zinc Hydrato-carbonate.	Dissolves with effervescence in diluted nitric acid (proof of carbonate). The solution gives with ammonium carbonate a white precipitate entirely soluble without colour in an excess of the reagent, forming a solution which is precipitated white by ammonium sulphide. The solution also gives a white precipitate with potassium ferrocyanide (proofs of zinc).	The absence of a red precipitate with ammonium carbonate indicates freedom from iron, as also the pure white with potassium ferrocyanide. The nitric acid solution should be free from sulphates and chlorides, and should give no colour with sulphuretted hydrogen.
Ferri Carbonas Saccharata. FerrousCarbonate containing Ferric.	Dissolves with effervescence in hydrochloric acid (proof of carbonate), and the solution gives a blue precipitate with both potassium ferrocyanide and potassium ferricyanide.	Volumetric analysis (which see).

Plumbi Carbonas. Plumbic Hydrato-carbonate.	Turned yellow by heat and blackened by sulphuretted hydrogen. Insoluble in water, soluble with effervescence in diluted acetic acid without leaving any residue, and forming a solution which is precipitated white by sulphuric acid, and yellow by potassium iodide (proofs of lead).	The acetic solution when treated with excess of sulphuretted hydrogen, boiled and filtered, gives no precipitate with ammonium oxalate (absence of chalk).
Bismuthi Sub-carbonas. Bismuthyl. Carbonate.	Blackened by sulphuretted hydrogen; insoluble in water, but soluble with effervescence in nitric acid. If to nitric acid mixed with half its volume of distilled water as much bismuth carbonate be added as the acid will dissolve, one volume of this solution poured into twenty volumes of water will yield a white precipitate (bismuthyl nitrate).	When added to sulphuric acid coloured with sulphate of indigo, the colour of the latter is not discharged (absence of nitrate). The nitric acid solution gives no precipitate with diluted sulphuric acid or with solution of argentic nitrate (absence of lead and chlorides).
	9. SULPHIDES.	
Sulphur Sublimatum.	Heated in open vessels, it burns entirely away with a blue flame, and the evolution of sulphurous acid.	Entirely volatilized by heat, showing absence of earthy matter; does not redden moistened litmus paper (absence of H_2SO_4 or H_2SO_3). Solution of ammonium hydrate agitated with it, and filtered, does not on evaporation leave any residue (absence of arsenious sulphide).
Sulphur *[illegible]cipitatum.*	Same as *sulphur sublimatum.*	The entire volatility shows absence of calcium sulphate. It should be seen to be quite amorphous when examined under the microscope (absence of sublimed sulphur).
[illegible]tassa [illegible]urata. [illegible]ssium sulphide,	It forms a yellow solution with water, which has the odour of sulphuretted hydrogen, and evolves it freely on dropping into it excess of hydrochloric acid, sulphur being at the same time deposited (proof of poly-	About three-fourths of its weight are dissolved by rectified spirit (proof of proper percentage of sulphide).

Name.	Proof of Presence of the Proper Constituents.	Proof of Freedom from Impurities.
	Sulphides (*continued*).	
containing Hyposulphite and Sulphate.	sulphide). The acid fluid, when boiled and filtered, is precipitated yellow by platinic chloride, and white by barium chloride (proofs of potassium and a trace of sulphate).	
Ethiops Mineral. Mercuric Sulphide, with excess of Sulphur.	Heated, burns with a blue flame and smell of sulphurous acid, and then entirely volatilizes. Insoluble in heated hydrochloric acid alone, but dissolves on adding a crystal of potassium chlorate; and the solution gives the usual reactions of mercuric salts.	General analysis.
Vermilion. Mercuric Sulphide.	Like the above, only no burning off of free sulphur takes place.	General analysis—the entire volatility showing absence of red lead and other fixed impurities.
Antimonium Sulphuratum. Antimonious Sulphide with Oxide.	Dissolved by heated hydrochloric acid, with the evolution of sulphuretted hydrogen and the separation of a little sulphur. Boiled in water with potassium hydro-tartrate, the resulting solution of potassium antimonyl tartrate is precipitated orange-red with sulphuretted hydrogen.	Free sulphur is detected by digestion with carbon disulphide; and the presence of a little antimonious oxide is proved by extracting with tartaric acid and passing sulphuretted hydrogen. Also proper percentage of antimony by gravimetric quantitative analysis.
	10. SULPHITES and HYPOSULPHITES.	
Acidum Sulphurosum. Sulphurous Acid.	It gives no precipitate, or but a very slight one, with barium chloride, but a copious one if solution of chlorine be also added (due to the conversion of sulphurous into sulphuric acid).	Volumetric analysis for proper percentage of SO_2 (which see).
Sodium Hyposulphite.	A solution heated with hydrochloric acid gives a smell of sulphurous acid and a deposit of sulphur (proof of hyposulphite), and also gives a yellow flame (proof of sodium).	Proper strength by volumetric analysis (which see).

11. SULPHATES.

Acidum Sulphuricum. Sulphuric Acid.	It evolves much heat on the addition of water, owing to chemical action taking place, and the formation of definite hydrates, such as $H_2SO_4H_2O$ and $H_2SO_42H_2O$. When thus diluted it gives a copious precipitate with barium chloride (barium sulphate).	Evaporated in a platinum dish, it leaves little or no residue. When a solution of ferrous sulphate is carefully poured over its surface, there is no purple colour developed when the two liquids unite (absence of nitrous compounds). Diluted with six times its volume of distilled water, it gives no precipitate with sulphuretted hydrogen (absence of arsenic and lead).
Sodæ Sulphas. Sodium Sulphate.	The aqueous solution gives a yellow flame (proof of sodium), and a white precipitate with barium chloride (proof of sulphate).	Exposed to heat in a porcelain crucible, it loses 55·9 per cent. of water. Heated with a solution of potassium hydrate, no odour of ammonia gas is evolved, and no precipitate is formed.
Potassæ Sulphas. Potassium Sulphate.	The aqueous solution, acidulated with hydrochloric acid, is precipitated white by barium chloride (proof of sulphate), and yellow by platinic chloride (proof of potassium).	It should be neutral to test-paper (absence of potassium hydrosulphate), and should give no precipitate with ammonium oxalate (absence of calcium).
Calcis Sulphas. Calcium Sulphate.	Digested with water, the filtered solution gives faint precipitates both with ammonium oxalate and barium chloride (proofs of calcium and sulphate respectively).	General analysis.
Magnesiæ Sulphas. Magnesium Sulphate.	Its solution gives copious white precipitates with barium chloride (proof of sulphate), and with a mixed solution of ammonium hydrate, ammonium chloride, and sodium phosphate (proof of magnesium).	Its aqueous solution at ordinary temperatures is not precipitated by ammonium oxalate (absence of calcium). Nor should it give a brown precipitate with chlorinated lime or soda (absence of iron). Also strength by gravimetric quantitative analysis (which see).
-lphas. hate.	Its solution gives a precipitate with ammonium hydrate soluble in excess; and the subsequent addition of ammonium sulphide gives a white precipitate (proof	Its watery solution is not tinged purple by tincture of galls (absence of iron); and when acidulated with sulphuric or hydrochloric acid gives no precipitate with

Name.	Proof of Presence of the Proper Constituents.	Proof of Freedom from Impurities.
	Sulphates (*continued*).	
	of zinc). It also gives a white precipitate with barium chloride (proof of sulphate).	sulphuretted hydrogen (absence of lead). After it has been boiled for a few minutes with a little nitric acid, it yields with ammonium hydrate a white precipitate entirely soluble without colour in an excess of the reagent (absence of copper).
Cupri Sulphas. Cupric Sulphate.	The aqueous solution gives with barium chloride a white precipitate insoluble in hydrochloric acid (presence of sulphates), and a maroon-red precipitate with potassium ferrocyanide (showing copper).	If an aqueous solution of the salt be mixed with twice its volume of solution of chlorine, and solution of ammonium hydrate be added, the precipitate formed by the first addition of the ammonium hydrate will be dissolved by a further and sufficient addition of the alkali, and a violet-blue solution will be produced, leaving nothing undissolved (absence of iron).
Hydrargyri Sulphas. Mercuric Sulphate.	When treated with water, it turns yellow; and the filtered solution gives a white precipitate with barium chloride, while the insoluble matter dissolved in diluted hydrochloric acid gives the usual reactions of mercuric salts.	Entirely volatile by heat (absence of fixed impurities).
Alumen. Ammonium-aluminium Sulphate.	Its solution gives a gelatinous white precipitate with ammonium hydrate. It also gives with potassium or sodium hydrate a white precipitate soluble in an excess of the reagent (proofs of aluminium); and the mixture evolves ammonia gas, especially when heated. The aqueous solution gives an immediate precipitate with barium chloride (proof of sulphate).	Its solution does not acquire a blue colour from the addition of potassium ferrocyanide or ferricyanide (absence of iron).
Ferri Sulphas. Ferrous Sulphate.	The aqueous solution is clear, gives a white precipitate with barium chloride, an instantaneous blue one with potassium ferricyanide (showing a ferrous salt), and a nearly white or light blue one with potassium	It gives no precipitate with sulphuretted hydrogen (absence of copper, etc.).

	ferrocyanide (the precipitate is at first white, the blue tinge being rapidly produced).	
Liquor Ferri Persulphatis. A solution of Ferric Sulphate.	Diluted with ten volumes of water, it gives a white precipitate with barium chloride (showing sulphates), and a blue precipitate with potassium ferrocyanide (presence of ferric salt), but not with potassium ferricyanide (absence of ferrous iron); specific gravity, 1·441.	Gravimetric quantitative analysis (which see).
	12. NITRATES.	
Acidum Nitricum. Nitric Acid.	If it be poured over copper, dense red vapours are immediately formed (nitric peroxide gas); but if the acid be mixed with an equal volume of water, and then added to the copper, it gives off a colourless gas (nitric oxide), which acquires an orange-red colour as it mixes with the air (nitric peroxide), and which, if it be introduced into a solution of ferrous sulphate, communicates to it a dark purple or brown colour (owing to the formation of a nitrosyl compound of ferrous sulphate).	The boiling point of the acid is 250° F. If submitted to distillation, the product continues uniform throughout the process. It leaves no residue when evaporated to dryness. Diluted with 6 times its volume of water, it gives no precipitate with barium chloride (absence of sulphates) nor with argentic nitrate (absence of chlorides).
Acidum Nitro-hydrochloricum dilutum.	It gives a precipitate with argentic nitrate insoluble in nitric acid, and at the same time it will convert ferrous sulphate to the ferric state, and cause an immediate blue colour when added to a mixture of potassium iodide and starch paste. The dilute nitric acid, on the one hand, will not precipitate silver, while on the other the dilute hydrochloric acid will not liberate iodine, nor raise iron to the ferric state.	
nti Nitras. ıtic Nitrate.	The solution gives with hydrochloric acid a white curdy precipitate (argentic chloride), which darkens by exposure to light, and is soluble in solution of ammonium hydrate. A small fragment heated on charcoal	A solution, after treatment with excess of hydrochloric acid and filtration, should leave no residue on evaporation (absence of potassium nitrate).

NAME.	PROOF OF PRESENCE OF THE PROPER CONSTITUENTS.	PROOF OF FREEDOM FROM IMPURITIES.
	NITRATES (*continued*).	
	with the blowpipe, first melts and then deflagrates, leaving behind a dull white metallic coating (metallic silver).	
Liquor Hydrargyri Nitratis Acidus.	A colourless and strongly acid solution, which produces a yellow precipitate on the addition of solution of potassium hydrate in excess (mercuric oxide). If a crystal of ferrous sulphate be dropped into it, in a short time the salt of iron and the liquid in its vicinity acquire a dark colour (presence of nitrates). Specific gravity, 2·240.	Does not give any precipitate when a little of it is dropped into hydrochloric acid diluted with twice its volume of water (absence of mercurous nitrate).
Liquor Ferri Pernitratis.	A clear solution of a reddish-brown colour, slightly acid and astringent to the taste, gives a blue precipitate with potassium ferrocyanide (proof of iron—ferric). When to a little of it placed in a test-tube half its volume of pure sulphuric acid is added, and then a solution of sulphate of iron is poured on, the whole assumes a dark brown colour.	Gravimetric quantitative analysis (which see).
Bismuthi Subnitras. Bismuthyl Nitrate, or Bismuthic Oxynitrate.	A heavy white powder in minute crystalline scales, blackened by sulphuretted hydrogen (forming bismuthous sulphide), insoluble in water, but soluble in nitric acid mixed with half its volume of distilled water, forming a solution which, poured into water, gives a white precipitate (characteristic precipitate of $BiONO_3$). It forms with sulphuric acid diluted with an equal bulk of water a solution which is blackened by ferrous sulphate (presence of nitrates).	The nitric acid solution gives no precipitate with dilute sulphuric acid (absence of lead), nor with solution of argentic nitrate (absence of chlorides).

Plumbi Nitras. Plumbic Nitrate.	Its solution gives yellow precipitates with potassium iodide and with potassium chromate (proofs of lead). When tested with sulphuric acid it deposits a white precipitate, and the addition of a slip of copper foil produces red fumes.	
	13. CYANIDES.	
Acidum Hydrocyanicum dilutum. Hydrocyanic Acid.	A fluid drachm of it evaporated in a platinum dish leaves no fixed residue. Treated with a minute quantity of a mixed solution of sulphate and persulphate of iron, afterwards with potash, and finally acidulated with hydrochloric acid, it forms Prussian blue.	No impurities. It gives no precipitate with barium chloride (absence of sulphates), but with argentic nitrate it gives a white precipitate entirely soluble in boiling concentrated nitric acid (argentic cyanide, and absence of chlorides).
	14. FERROCYANIDES.	
Potassæ Prussias Flava. Potassium Ferrocyanide.	The aqueous solution precipitates deep blue with persulphate of iron (ferric ferrocyanide), brick-red with cupric sulphate (cupric ferrocyanide), and white with acetate of lead (plumbic ferrocyanide). Heated with dilute sulphuric acid, hydrocyanic acid vapours are evolved.	
	15. FERRICYANIDES.	
otassæ Prussias Rubra. otassium yanide.	The solution gives off hydrocyanic acid when heated with sulphuric acid. It also gives a deep blue with ferrous sulphate, but no blue with ferric chloride.	No blue with ferric sulphate shows absence of ferrocyanide.
	16. HYPOPHOSPHITES and PHOSPHATES.	
dæ hosphis. um sphite.	At a red heat it ignites, emitting spontaneously inflammable phosphuretted hydrogen. A platinum wire dipped in the solution gives a yellow flame (proof of sodium).	

Name.	Proof of Presence of the Proper Constituents.	Proof of Freedom from Impurities.
	Hypophosphites and Phosphates (*continued*).	
Calcis Hypophosphis. Calcium Hypophosphite.	Heated to redness, it ignites, evolving spontaneously inflammable phosphuretted hydrogen, and leaving a reddish-coloured residue amounting to about 80 per cent. of the salt. A solution treated with oxalic acid not quite in excess gives a white precipitate (presence of Ca), and after filtration the solution boiled with cupric sulphate gives a reddish deposit (metallic Cu, indicating presence of hypophosphate).	
Acidum Phosphoricum dilutum. Phosphoric Acid.	With ammonio-nitrate of silver it gives a canary yellow precipitate, soluble in ammonium hydrate and in diluted nitric acid (proof of phosphate). Evaporated it leaves a residue, which melts at a low red heat, and upon cooling exhibits a glassy appearance (metaphosphoric acid).	It is not precipitated by sulphuretted hydrogen (absence of metals), barium chloride (absence of sulphates), or argentic nitrate (absence of chlorides). When mixed with an equal volume of pure sulphuric acid, and then introduced into a solution of ferrous sulphate, it does not communicate a dark colour (absence of nitrates). Mixed with an equal volume of solution of mercuric chloride and heated, no precipitate is formed (absence of phosphorous acid). Also volumetric and gravimetric quantitative analysis (which see).
Ammoniæ Phosphas. Diammonium Hydrogen Phosphate.	Heated, it gives off ammonia, and gives a glassy residue which is acid to test-paper. With argentic nitrate its solution gives a canary yellow (proof of phosphate).	
Sodæ Phosphas. Disodium Hydrogen Phosphate.	It imparts a yellow colour to flame (proof of sodium). Its solution has a faintly alkaline reaction, it gives a yellow precipitate with argentic nitrate, the resulting fluid acquiring an acid reaction (proof of phosphate).	Heated to dull redness it loses 63 per cent. of its weight, leaving a residue, which, when dissolved in water, gives with barium chloride a precipitate almost entirely soluble in diluted nitric acid (presence of a trace only of sulphates).

Calcii Phosphas. Calcium Phosphate.	It is soluble without effervescence in diluted nitric acid. The solution continues clear when an excess of sodium acetate is added to it, but lets fall a white precipitate on the subsequent addition of ammonium oxalate (presence of calcium), or of ferric chloride (presence of PO_4).	It is soluble in acetic acid, which distinguishes it from calcium oxalate. It is separated from aluminium, in an incomplete way, by dissolving in hydrochloric acid and precipitating with excess of potassium hydrate (in which the aluminium hydrate is soluble). Also gravimetric quantitative analysis (which see).
Ferri Phosphas. Ferrous Phosphate.	Soluble in hydrochloric acid. The solution yields a precipitate with both potassium ferrocyanide and ferricyanide: that afforded by the latter being the more abundant (showing that although chiefly ferrous a slight change to ferric has taken place); and when treated with tartaric acid and an excess of ammonia, and subsequently with the solution of ammonio-sulphate of magnesia, lets fall a crystalline precipitate (presence of phosphate).	When the salt is digested in hydrochloric acid with a lamina of pure copper, a dark deposit does not form on the metal (absence of arsenic). Also volumetric quantitative analysis (which see).
	17. ARSENITES AND ARSENIATES.	
Acidum Arseniosum. Arsenious Acid.	When slowly sublimed in a glass tube, it forms minute brilliant and transparent octahedral crystals. It is sparingly soluble in water, and its solution gives with ammonio-nitrate of silver a canary-yellow precipitate insoluble in water, but readily dissolved by ammonium hydrate and by nitric acid. Sprinkled on a red-hot coal, it emits an alliaceous odour. It is entirely volatilized at a temperature not exceeding 400°.	Volumetric quantitative analysis (which see).
rsenias. dium arseniate.	Soluble in water; the solution is alkaline, giving white precipitates with chloride of barium, chloride of calcium, and sulphate of zinc, and a brick-red precipitate with nitrate of silver, all of which are soluble in nitric acid.	Heated to 300° it loses 40·38 per cent. of its weight (proper amount of water of crystallization). Also volumetric quantitative analysis (which see).

NAME.	PROOF OF PRESENCE OF THE PROPER CONSTITUENTS.	PROOF OF FREEDOM FROM IMPURITIES.
	ARSENITES AND ARSENIATES (*continued*).	
Ferri Arsenias. Ferrous Arseniate.	Readily dissolved by hydrochloric acid. This solution gives a copious light-blue precipitate with potassium ferrocyanide, and a still more abundant one of a deeper colour with potassium ferricyanide. A small quantity boiled with an excess of sodium hydrate and filtered, gives, when exactly neutralized by nitric acid, a brick-red precipitate on the addition of solution of argentic nitrate.	The solution in hydrochloric acid when diluted gives no precipitate with barium chloride.
	18. BORATES.	
Borax.	A little of the powdered salt is placed on a crucible lid and moistened with strong sulphuric acid. Some spirit of wine is then added, and the whole having been stirred with a glass rod, a light is applied. The flame of the burning spirit is tinged yellow externally (proof of sodium), and green internally (proof of boracic acid).	Qualitative analysis and also volumetric quantitative analysis for alkalinity. 19·1 grammes taking 100 cc. oxalic acid for neutralization.
	19. ACETATES.	
Acidum Aceticum. Acetic Acid.	Known by its peculiar smell and acid reaction.	It leaves no residue when evaporated (absence of metallic and other fixed impurities), and gives no precipitate with sulphuretted hydrogen (absence of metals), barium chloride, or silver nitrate (absence of sulphuric or hydrochloric acids). If a fluid drachm of it, mixed with half an ounce of distilled water and half a drachm of pure hydrochloric acid, be put into a small flask with a few pieces of granulated zinc, and while the effervescence continues a slip of bibulous paper wetted with solution of plumbic subacetate be suspended in the upper part of the flask above the

		liquid for about five minutes, the paper will not become discoloured. (This shows absence of sulphurous acid, which, by the action of the nascent hydrogen, would be converted into sulphuretted hydrogen, and stain the lead black, forming PbS.) Also volumetric quantitative analysis (which see).
Sodæ Acetas. Sodium Acetate.	The solution gives a yellow flame (proof of sodium), and a red colour with ferric chloride, bleached by the slightest excess of hydrochloric acid. Heated with sulphuric acid and rectified spirit, it evolves the smell of apples (proofs of acetate).	It should not affect test-paper (absence of excess of acid or alkali). It should give no precipitate with argentic nitrate or barium chloride (absence of sodium or calcium chlorides or sulphates).
Potassæ Acetas. Potassium Acetate.	With a watery solution, tartaric acid causes a crystalline precipitate (proof of potassium); sulphuric acid the disengagement of acetic acid; and a dilute solution of ferric chloride, a deep red colour (proofs of acetate).	Neutral to test-paper, no effervescence with acids, entirely soluble in rectified spirit (absence of potassium carbonate). Its solution is unaffected by ammonium sulphide (absence of iron and heavy metals generally).
Zinci Acetas. Zinc Acetate.	Evolves acetic acid when decomposed by sulphuric acid; soluble in water, and the solution precipitated pure white by ammonium sulphide.	A dilute watery solution is not affected by barium chloride or argentic nitrate (absence of sulphates and chlorides); and, when slightly acidulated with hydrochloric acid, is not precipitated by sulphuretted hydrogen (absence of lead and arsenic); after it has been boiled for a few minutes with a little nitric acid, it yields with ammonium hydrate a white precipitate entirely soluble without colour in an excess of the reagent (absence of iron).
Plumbi Acetas. Plumbic Acetate.	Its solution gives a yellow precipitate with potassium iodide, and is precipitated white by sulphuric acid (plumbic sulphate), acetic acid being set free. Its solution in distilled water is clear, or has only a slight milkiness, which disappears on the addition of acetic acid.	Volumetric quantitative analysis (which see).

Name.	Proof of Presence of the Proper Constituents.	Proof of Freedom from Impurities.
	Acetates (*continued*).	
Liquor Plumbi Subacetatis. Plumbic Oxyacetate Solution.	It is alkaline to test-paper, and forms with mucilage of gum arabic an opaque white jelly. Sulphuric acid in excess gives a white precipitate, acetic acid being set free.	Volumetric quantitative analysis (which see). The liquor may contain general impurities or be too weak. Specific gravity.
	20. VALERIANATES.	
Sodæ Valerianas. Sodium Valerianate.	Gives a yellow flame, and a smell of valerian when heated with sulphuric acid.	Is neutral to test-paper and soluble in spirit (absence of sodium hydrate and carbonate).
Zinci Valerianas. Zinc Valerianate.	Heated with sulphuric acid, evolves the odour of valerian. Heated to redness in an open crucible, it leaves a residue which, when dissolved in diluted sulphuric acid, yields with ammonia a precipitate which entirely dissolves in an excess of the reagent, and the resulting solution gives a white precipitate with sulphide of ammonium.	Its solution in hot water is not precipitated by chloride of barium (absence of sulphates). It gives when heated with diluted sulphuric acid a distillate, which when mixed with the solution of acetate of copper, does not immediately affect the transparency of the fluid, but forms after a little time oily drops, which gradually pass into a bluish-white crystalline deposit (absence of butyric acid).
	21. OXALATES.	
Acidum Oxalicum. Oxalic Acid.	Entirely volatile when heated below 350° Fah. Its solution, neutralized by ammonium hydrate, gives a white precipitate with calcium chloride, insoluble in acetic acid but soluble in hydrochloric acid.	Does not discharge the colour of a very dilute solution of indigo sulphate when boiled with it (absence of nitric acid).
Ammonium Oxalate.	Entirely volatile by heat. Gives off a smell of ammonia when boiled with potassium hydrate, and also gives a white precipitate with calcium chloride insoluble in acetic acid.	(Absence of fixed impurities.)
Cerii Oxalas. Cerium Oxalate.	Decomposed at a dull red heat into a reddish-brown powder, which dissolves completely and without effervescence in boiling hydrochloric acid; and the resulting	If the salt be boiled with potassium hydrate and filtered, the filtrate is not affected by solution of ammonium chloride (absence of alumina). The fact of

	solution gives, with solution of potassium sulphate, a white crystalline precipitate. If boiled with potassium hydrate and filtered, the solution, supersaturated with acetic acid, gives with chloride of calcium a white precipitate, which is soluble in hydrochloric acid (proof of oxalate).	the ignited salt not effervescing with hydrochloric acid indicates the absence of carbonates and of foreign fixed oxalates in the unignited salt.
	22. TARTRATES.	
Acidum Tartaricum. Tartaric Acid.	It has a strongly acid taste, and is readily soluble in water and in rectified spirit. When to either solution, not too much diluted, a little acetate of potash is added, a white crystalline precipitate is formed.	An aqueous solution of the acid is not affected by sulphuretted hydrogen, and gives no precipitate with the solution of sulphate of lime or of oxalate of ammonia. It leaves no residue, or only a mere trace, when burned with free access of air. Also volumetric analysis (which see).
Potassæ Tartras Acida. Potassium Hydro-tartrate.	Heated in a crucible, it evolves inflammable gas and the odour of burnt sugar; and leaves a black residue. This effervesces with diluted hydrochloric acid, and forms a solution which when filtered gives a yellow precipitate with platinic chloride (proof of potassium).	The ash also forms with hydrochloric acid a solution which, when neutralized by ammonium hydrate, is rendered slightly turbid by ammonium oxalate (presence of calcium, indicating a slight contamination of the salt under examination by calcium tartrate); but it should not give the slightest precipitate with potassium chromate (absence of barium). Also volumetric analysis (which see).
Potassæ Tartras. Potassium Tartrate.	Heated with sulphuric acid, it forms a black tarry fluid, evolving inflammable gas (carbonic oxide and sulphurous anhydride) and the odour of burned sugar. Acetic acid added sparingly to its solution causes the separation of a white crystalline precipitate (potassium hydrogen tartrate).	Entirely dissolved by its own weight of water (absence of cream of tartar). Also volumetric analysis (which see).
Soda Tartarata. Potassium Sodium Tartrate.	Heated with sulphuric acid it blackens, evolving inflammable gases and the odour of burnt sugar. It imparts a yellow colour to flame. A strong solution gives a crystalline precipitate with a small quantity of	Volumetric analysis (which see).

NAME.	PROOF OF PRESENCE OF THE PROPER CONSTITUENTS.	PROOF OF FREEDOM FROM IMPURITIES.
	TARTRATES (*continued*).	
	acetic acid (potassium hydrogen tartrate). Entirely soluble in cold water.	
Antimonium Tartaratum. Potassium Antimonyl Tartrate.	It blackens when heated with sulphuric acid. Its solution gives a white cloud with hydrochloric acid, which is soluble in excess, and the resulting liquid is precipitated orange by sulphuretted hydrogen.	Gravimetric quantitative analysis (which see).
	23. CITRATES.	
Acidum Citricum. Citric Acid.	Blackens slowly when heated with sulphuric acid. Its solution, neutralized by ammonium hydrate and cooled, gives no precipitate with calcium chloride until it has been boiled for a time.	The aqueous solution is not darkened by sulphuretted hydrogen (absence of metals), gives no precipitate when added in excess to solution of acetate of potash (absence of tartaric acid), or of chloride of barium (absence of sulphates), and if sparingly added to cold limewater it does not render it turbid. The crystals leave no ash when burned with free access of air. Also volumetric analysis (which see).
Lithiæ Citras. Lithium Citrate.	Heated to redness it blackens, evolving inflammable gases; and the residue, neutralized by hydrochloric acid, yields with rectified spirit a solution which burns with a crimson flame (proof of lithium).	Quantitative analysis (which see).
Potassæ Citras. Potassium Citrate.	Heated with sulphuric acid it forms a brown fluid, gives off an inflammable gas, and evolves the odour of acetic acid. Its solution, mixed with a solution of chloride of calcium, remains clear till it is boiled, when a white precipitate separates (calcium citrate), readily soluble in acetic acid. Its solution, acidulated with hydrochloric acid, gives a yellow precipitate with perchloride of platinum (presence of potassium).	Volumetric analysis (which see).

Liquor Bismuthi Citratis. Bismuth and Ammonium Citrate.	Neutral or slightly alkaline to test-paper; mixes with water without change; heated with solution of potash it evolves ammonia, and yields a white precipitate (bismuthous hydrate). Hydrochloric acid added to it gives a white precipitate, which is soluble in excess of the reagent.	Gravimetric quantitative analysis (which see).
	24. SCALE PREPARATIONS.	
Ferrum Tartaratum. Potassium Ferric Tartrate.	The aqueous solution acidulated with hydrochloric acid is precipitated blue by potassium ferrocyanide, but not by ferricyanide (proof of ferric iron). Boiled with potassium hydrate, a precipitate of ferric hydrate separates, and potassium tartrate is left in solution. On pouring off a little of this liquid when clear, cooling thoroughly, and acidulating with acetic acid, a precipitate of cream of tartar slowly separates (proof of tartrate). When ignited till fumes cease, the ash is alkaline to moistened test-paper, and when extracted by a small quantity of water, and the solution acidulated with hydrochloric acid, a yellow precipitate forms on the addition of platinic chloride (proof of potassium).	When boiled with potassium hydrate no ammonia should be evolved (distinction from the common commercial scale, which contains NH_3). Also yields 30 per cent. Fe_2O_3 by ignition, washing the ash with water, and collecting, igniting, and weighing the insoluble matter.
Ferri et Ammoniæ Citras. Ammonium Ferric Citrate.	Ignited it leaves only Fe_2O_3 insoluble in water and not alkaline. Boiled with potassium hydrate it evolves ammonia gas (proof of NH_3), deposits ferric hydrate, and leaves potassium citrate in solution. On cooling a portion of this clear liquid, neutralizing carefully with acetic acid, then adding calcium chloride and a slight excess of ammonium hydrate, a precipitate is obtained only on boiling (proof of citrate). The aqueous solution of the scale, acidulated with HCl, gives a blue	When the alkaline liquid is acidulated with acetic acid and cooled, no precipitate should form (absence of tartaric acid). The ash should be pure—Fe_2O_3—and should amount to 27 per cent.

NAME.	PROOF OF PRESENCE OF THE PROPER CONSTITUENTS.	PROOF OF FREEDOM FROM IMPURITIES.
	SCALE PREPARATIONS (*continued*). precipitate with potassium ferrocyanide, but none with ferricyanide (proof of ferric iron).	
Ferri et Quiniæ Citras. Ammonium, Quinine, and Ferrous-ferric Citrates.	The solution gives with a *slight* excess of ammonium hydrate a white precipitate of hydrated quinia, which, disappears on shaking up with pure ether. The ethereal liquid separated by a pipette, and evaporated to dryness at a *very gentle* heat, leaves a residue which, dissolved in water by the aid of a drop of hydrochloric acid, gives a deep green colour on the successive addition of chlorine water and ammonium hydrate (proof of *quinia*). The aqueous solution of the scale gives a blue with both the ferro- and ferri-cyanides of potassium (proof of iron both in the ferrous and ferric states). Boiled with potassium hydrate, it gives proof of the citrate, exactly as already described in *Ferri et Ammoniæ Citras.*	The quinia precipitable by the slightest possible excess of ammonium hydrate. When collected on a weighed filter, slightly washed with cold water, and dried, should weigh 16 per cent.
Beberiæ Sulphas. Beberine Sulphate.	Its watery solution gives a white precipitate with barium chloride (presence of sulphates), and with sodium hydrate a yellowish-white precipitate (the alkaloid itself) which is dissolved by agitating the mixture with twice its volume of ether. The ethereal solution, separated by a pipette and evaporated, leaves a yellow translucent residue, entirely soluble in dilute acids.	Entirely destructible by heat (absence of fixed impurities).

CHAPTER V.

QUALITATIVE ANALYSIS, AS APPLIED TO THE DETECTION OF UNKNOWN SALTS.

I. GENERAL PRELIMINARY EXAMINATION.

Under this head are included, –

1. The observation of the physical properties of the substance submitted for analysis.
2. Its behaviour when heated, either alone or in the presence of reducing agents or fluxes.
3. Its reaction with test papers; the colour it communicates to flame, etc.

So particular and minute may this examination be, that in the larger works on chemical analysis many pages will be found devoted to it; but for the purposes of the analysis likely to come before the ordinary chemical student, it is sufficient to only carry it the length of a few readily obtainable and unmistakable inferences. In discussing the appearances to be obtained and the inferences to be drawn, we will take two distinct cases:—

First, the best method of procedure in event of the substance being a **fluid**; and,—

Second, in the event of its being a **solid**.

Case I. THE SUBSTANCE GIVEN IS A FLUID.

Step 1. Carefully mark its reaction with blue and red litmus paper. Evaporate a little to dryness at a gentle heat on a clean porcelain crucible lid, observing the nature of the residue left, if any; and finally raise this residue to a red heat, carefully noting whether it is volatilized, blackened, or altered in colour any way.

From a careful study of these points, the following simple inferences may safely be drawn, any appearance not referred to being neglected as not affording a really distinctive indication.

A. **Neutral,** no odour, and leaving **no residue** whatever. Probably water.

B. **Strongly acid,** leaving **no residue.** Probably an ordinary volatile acid, such HCl, HNO_3, $HC_2H_3O_2$, etc.

C. **Strongly acid,** leaving **a residue,** fusible by heat and also strongly acid. Probably a non-volatile mineral acid, such as H_3PO_4.

D. **Strongly acid,** leaving **a residue,** which on heating **chars,** and entirely burns away. Probably free organic acid, such as $H_2C_4H_4O_6$, $H_3C_6H_5O_7$, $HC_7H_5O_2$, etc.

E. **Neutral or slightly acid,** leaving **a residue,** which volatilizes in fumes, but without blackening. Probably an ordinary salt of a volatile metal, such as NH_4, Hg, As, Sb, etc.

F. **Neutral or slightly acid,** leaving **a residue,** which on heating blackens and volatilizes in fumes. Probably an organic salt of NH_4, Sb, or other volatile metal.

G. **Neutral or slightly acid,** leaving **a residue,** which on heating changes colour as follows:—

Yellow while hot, white on cooling, Probably salt of Zn.

Deep yellow while hot, yellow on cooling. Probably salt of Pb.

Yellowish-brown while hot, dirty light-yellow on cooling. Probably salt of Sn^{IV}.

Orange or red while hot, dull-yellow on cooling. Probably salt of Bi.

Red while hot, reddish-brown on cooling. Probably salt of Fe or Ce.

Permanent brownish black. Certain salts of Mn.

H. **Neutral or slightly acid,** leaving **a white residue,** which blackens on heating, burns, and leaves a black or greyish mass. Probably an organic salt of a fixed metal. *In this special case, proceed as follows:*

Moisten the residue with a little water, and touch it with reddened litmus paper. If alkaline, the original substance was an organic salt of K, Na, or Li, in which case proceed by (*a*). If not alkaline, proceed by (*b*).

(*a*) Boil the ash with the smallest possible quantity of water, filter, acidulate with HCl till effervescence ceases; dip a perfectly clean platinum wire in the solution, and try the flame test. If crimson, Li. Bright yellow, Na. Violet, K.

Note.—The latter flame not being very easily seen in daylight, it is advisable to add to the solution $PtCl_4$ and C_2H_6O. Shake well and cool. Yellow crystalline precipitate of potassium platinochloride ($PtCl_4 2KCl$).

(*b*) The ash is covered with water and treated with $HC_2H_3O_2$. If effervescence takes place, the original substance was probably an organic salt of Ba, Sr, or Ca; and these metals may at once be tested for in the acetic acid solution.

I. **Neutral or slightly acid,** leaving **a residue** which takes fire and continues to burn even after removal from the flame, giving off clouds of white fumes and leaving a fixed white or pinkish residue. Probably a hypophosphite; which fact should be noted as an aid to future information as to acidulous radicals.

K. **Strongly alkaline,** leaving a fixed white residue, **also alkaline.** A hydrate, carbonate, bicarbonate, or sulphide of a fixed alkaline metal, or a hydrate or oxide of Ba, Sr, or Ca. In this case proceed as follows:—

Acidulate a portion of the original solution with HCl.

(*a*) If it effervesces without smell, and is therefore a carbonate or bicarbonate, test at once by the flame for K, Li, Na, and also another portion of the original solution with $HgCl_2$. If red, a carbonate; if not, a bicarbonate.

(*b*) Effervesces with smell of H_2S. In this case it is a sulphide; and if a deposit of S also takes place, a polysulphide. Add to a fresh portion of the original solution excess of HCl, boil till H_2S is expelled, filter, if necessary, and test the solution for all metals of fourth and fifth groups.

(*c*) It does not effervesce. In this case add to a fresh portion of the original solution, $AgNO_3$. If a brownish-black precipitate be formed, it is a soluble hydrate. A portion of the original solution should be neutralized with HCl, and then examined for all metals of fourth and fifth groups.

Note.—If $AgNO_3$ with original solution gives a yellow, a white, or a brick-red precipitate, the presence of a phosphate, borate, or arseniate of K or Na may be suspected. In the case of a complex solution in which a salt of some other metal is given dissolved in excess of an alkali, an intimation of the fact will be obtained on cautiously adding the HCl, as, at the moment of neutralization, the dissolved substance appears as a precipitate before again dissolving in the excess of HCl. Basic plumbic acetate has an alkaline reaction.

2. Dip a clean platinum wire in the solution, and heat in the inner Bunsen or blowpipe flame. The outer flame is coloured as under :—

Violet . . .	Potassium.
Golden-yellow .	Sodium.
Yellowish green .	Barium.
Crimson . .	Strontium or Lithium.
Orange-red . .	Calcium.
Green . . .	Copper or Boracic Acid.
Blue . . .	Lead, Arsenic, Bismuth; also Copper as chloride.

Case II. THE SUBSTANCE GIVEN IS A SOLID.

1. Heat a little of the substance to redness on platinum foil.

A. It fuses and gives off steam, probably water of crystallization.

B. It fuses and gives off the odour of ammonia, and leaves an acid residue, probably the ammoniacal salt of a fixed acid as $(NH_4)_2HPO_4$.

C. It volatilizes without blackening, probably an ordinary salt of NH_4, Hg, As, Sb.

Note.—Sb_2O_3 fuses to a yellow mass before volatilizing. Many iodides also fuse and give off iodine in violet fumes, especially PbI_2 and CdI_2.

D. Blackens, burns, and volatilizes. A free organic acid, or an organic salt of NH_4, Hg, As, or Sb.

Note.—Oxalates, although organic, do not blacken to any extent. If carefully observed, however, a slight greyish tint, followed by a distinct glow running through the mass, will be noticed at the moment of decomposition. To make certain, it is well to place a little of the original powder in one tube, and the residue, after ignition, in another; cover them both with water, and add a drop of acetic acid to each. If the residue effervesce, and the original powder does not, strong presumptive evidence is obtained of the presence of an oxalate of the alkaline or earthy metals.

E. Blackens, burns, and leaves a fixed residue, an organic salt of a fixed metal. Examine residue as per Case I. Step 1, *H*.

F. The substance does not blacken, but changes colour. See Case I, Step 1. *G*.

Step 2. Heat a little of the substance on charcoal before the blowpipe.

Ordinary alkaline salts fuse and sink into the charcoal. Some decrepitating (example NaCl, etc.), others deflagrating (as KNO_3, $KClO_3$, etc.), but no sufficiently characteristic indications are usually obtained, except in one of the following cases:—

A. A white luminous residue is left. Moisten it when cold with a drop or two of cobaltous nitrate, and again apply the blowpipe, observing any change of colour as follows:—

The residue becomes blue, indicating Al, Silicates, or Phosphates.

" " " green, " Zn.

" " " pink or flesh-coloured, indicating Mg.

B. A coloured residue is left. Prepare a borax bead, and heat a litttle of the substance in it, both in the reducing and oxidizing flame, and note any colours corresponding with the following list.

Metal.	In Oxidizing Flame.	In Reducing Flame.
Cu	Green (hot). Blue (cold).	Red (cold).
Co	Blue.	Blue.
Cr	Green.	Green.
Fe	Red (hot). Yellowish (cold).	Bottle-green.
Mn	Amethyst.	Colourless.
Ni	Reddish-brown (hot). Yellow (cold).	Same as oxidizing flame.

C. A metallic residue is left, with or without incrustation surrounding it. Mix a little of the substance with KCy and Na_2CO_3, and expose on charcoal to the reducing charcoal flame.

(*a*) Metallic globules are produced without any surrounding incrustation of oxide. This occurs with Ag, Au, Cu, Fe, Co, and Ni, all easily recognisable.

(*b*) Metallic globules are produced with a surrounding incrustation of oxide. This occurs with Sn, Bi, Pb, and Sb. The incrustation having the characteristic colours already described in Case I., Step 1, *G*.

Note.—Sb often forms a white and distinctly crystalline crust.

(*c*) The metal volatilizes, and only leaves an incrustation of oxide. This occurs with As (garlic smell and white incrustation), Zn (yellow [hot], white [cold]), and Cd (reddish-brown).

Step 3. Dip a clean platinum wire in HCl, then in the substance, and heat in the inner Bunsen or blowpipe flame; and observe effects already noticed in Case I., Step 2.

I. PREPARATION OF THE SOLUTION FOR ANALYSIS FOR METALS, IF THE SUBSTANCE BE NOT ALREADY DISSOLVED.

1. Take a minute portion of the substance and boil it with water in a test-tube; should it dissolve, then take a larger portion and dissolve for testing.
2. Should the salt prove insoluble, take another small portion and heat with HCl, and add a little water and again heat. If it now dissolves, prepare a larger quantity of the solution for use in the same manner.
3. Should it resist HCl, try another small portion with HNO_3 by heating, and then adding water. If this dissolves it, make up a larger quantity of a similar solution for testing.
4. Should HNO_3 also fail, try another small portion with two parts HCl and one part HNO_3, warming and diluting as before; and if it succeeds, make up a larger amount of solution in the same manner.
5. If all acids fail, then take another portion of the substance, mix it with several times its bulk of a perfectly dry mixture of sodium and potassium carbonates (prepared by heating Rochelle salt in an open crucible until the residue thoroughly ceases to evolve any gases, then extracting with distilled water, filtering, evaporating to dryness, heating the residue to redness, and preserving for use in a stoppered bottle. This reagent will hereafter be shortly described as **fusion mixture**). Place the whole in a platinum crucible, and fuse at a bright-red heat; when cold, boil with water and save the solution thus obtained for acidulous radicals. The insoluble matter is then to be drenched with strong HCl, slightly diluted and boiled, and the solution used for testing for the metal. Any insoluble white gritty matter still remaining is put down as silica.

III. DETECTION OF THE METAL.

The processes to be applied vary according as the substance under examination is a simple salt or a mixture of salts; and the following tables are to be used accordingly.

Table for the Detection of the Metal in a Solution containing one Base only.

using this Table, as soon as the Metal is discovered we go no further, and all confirmations, except where specially stated, are to be applied to portions of the original Solution, hereafter represented by O.

1st Group.—Add a drop of HCl, and if it produce a precipitate, add excess.

1st Group	2nd Group	3rd Group (Division A)	3rd Group (Division B)	4th Group	5th Group
	2nd Group. To solution in which a drop of HCl has failed to produce a ppt. add H_2S, and if a discoloration appear, add excess and warm.	3rd Group (Division A). Evaporate a portion of original solution to dryness, and heat residue till any organic matter is destroyed; then dissolve in a few drops of HCl with the addition of a drop or two of HNO_3, dilute, and add NH_4Cl, and then NH_4HO in slight but distinct excess, and heat to boiling.	3rd Group (Division B).—To the solution in which NH_4HO has failed to produce a precipitate, add NH_4HS, and warm for some time.	4th Group.—To same solution, add $(NH_4)_2CO_3$.	5th Group.
Precipitate May be either $PbCl_2$, Hg_2Cl_2, $AgCl$ } White. Confirmations. Let ppt. settle, and pour off supernatant liquid; wash once by decantation with *cold* water, and then proceed as follows;— (1.) Add some warm H_2O to ppt. and boil: if it dissolves and the solution gives a yellow with K_2CrO_4 = Pb. (2.) If ppt. insoluble in water, add to it excess of NH_4HO. (*a*) The precipitate turns black Hg_2 (ous). (*b*) The precipitate dissolves and is re-precipitated by HNO_3 = **Ag**.	Precipitate May be either HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, Sb_2S_3, SnS, SnS_2, PtS_2 or Au_2S_3 Let the precipitate settle, pour off as much of the supernatant liquid as possible, make the remainder alkaline by NH_4HO and add a few drops of NH_4HS and warm. Insoluble. CdS—yellow HgS, PbS, Bi_2S_3, CuS } Blackish Soluble. As_2S_3, SnS_2 } Yellow. Sb_2S_3—Orange SnS, PtS_2, Au_2S_3 } Blksh. Confirmations. (1.) *If ppt. yellow and insoluble in NH_4HS.*—Cd. (2.) *If ppt. black and insoluble in NH_4HS.* (*a*) Add to O, H_2SO_4 : white—Pb. (*b*) Add to O, KHO: yellow—**Hg**; white—**Bi**; and blue=Cu. (3.) *If ppt. yellow and soluble in NH_4HS.*	*Precipitate May be either $Fe_2 6HO$ = red-brown. $Cr_2 6HO$ = green. Ce2HO, $Al_2 6HO$, Insol. phosph. of Fe, Cr, Al, Mn, Ba, Sr, Ca, and Mg. } White. Confirmations. (I.) *If ppt. red.* (*a*) Test O with $K_6Fe_2Cy_{12}$: dark blue = Fe. (*b*) Test O with K_4FeCy_6 : dark blue = Fe_2. (II.) *If ppt. green.* Evap. portion of O on a porcelain crucible lid, add some KHO and a crystal of KNO_3, again evap. to dryness and fuse: yellow residue, sol. in H_2O and precipitated yellow by Pb_2Ac after acidulation by HAc = Cr. (III.) *If ppt. white.* (1.) Add to O, KHO; white sol. in excess and re-precipitated by boiling with NH_4Cl = Al.	Precipitate May be either MnS—flesh colrd. ZnS—white. CoS, NiS } black. Confirmations. I. *If ppt. white or flesh-coloured.* (1.) Test O by evaporating & fusing with KHO and KNO_3: green residue—Mn. (2.) Test O with K_4FeCy_6 : white—Zn. II. *If ppt. be black,* boil O with KHO. (*a*) Blueish ppt. turning pinkish on boiling Co.	Precipitate May be either $BaCO_3$, $SrCO_3$, $CaCO_3$ } White Confirmations. Let ppt. settle, pour off as much supernatant liquor as possible, and dissolve in HAc, then test successively in the same liquid. (1.) With K_2CrO_4: yellow—**Ba**. (2.) With a drop of dilute H_2SO_4 and let it stand: white=Sr.	— (1). Divide into two portions; test one with Na_2HPO_4 : white=**Mg**. (2.) Evaporate the remainder to dryness, heat till fumes cease, dissolve residue in the smallest possible quantity of water, and try the flame test. (*a*) Crimson flame = Li. (*b*) Violet flame = **K**.

	(*a*) Add to O, KHO: white (sol. in excess and not re-precipitated on boiling)=**Sn** (ic). (*b*) Add to O, KHO and Zn, boil and hold paper moistened with $AgNO_3$ over the tube: black stain=**As**. (4.) *If ppt. orange, soluble in* NH_4HS, and re-precipitated orange by HCl=**Sb**. (5.) *If ppt. brown or black, and soluble in* NH_4HS. (*a*) Add to O, $HgCl_2$ and boil: grey=**Sn** (ous.) (*b*) Add to O, $SnCl_2$: purple=**Au**. (*c*) Add to O, KCl and S.V.R.: yellow=**Pt**.	(2.) *If ppt. with KHO be insoluble in excess*, test O with $(NH_4)_2MoO_4$ dissolved in HNO_3 and boil. (*a*) *If no precipitate forms*, test O for **Ce** by evaporating and igniting and getting a red residue, which dissolves with difficulty in strong HCl, and the solution diluted and nearly neutralized gives a white with $(NH_4)_2C_2O_4$. (*b*) *If a yellow precipitate forms*, phosphoric acid is present, in which case proceed as follows:—Add to O, NH_4HO in excess, and then HAc until the solution is acid and boil. (A) *A ppt. forms*, it may be $FePO_4$, $CrPO_4$, or $AlPO_4$, filter, wash, and treat on filter with boiling dilute KHO. * *A reddish residue is left on filter*=**Fe** (test O for Fe and Fe_2. † *A greenish residue is left on filter*=**Cr** (fuse as above.) ‡ *The ppt. dissolves*=**Al** (confirm by boiling filtrate with NH_4Cl.) (B) *No precipitate forms.* We may have in solution the phosphates of Ba, Sr, Ca, Mn, or Mg. Test the same solution with K_2CrO_4: yellow=**Ba**. If no effect add a drop or two of dilute H_2SO_4, and stand for a short time: white=**Sr**. If not Sr add $(NH_4)_2C_2O_4$: white=**Ca**. If still not Ca cool and add excess of NH_4HO: white=**Mg** or **Mn**. Fuse ppt. on porcelain with KHO and KNO_3: green residue=**Mn**. If no green then the ppt. was **Mg**.	(*b*) Greenish ppt. unaltered by boiling =**Ni**. (Both should be confirmed by blowpipe bead.)	(3.) With $(NH_4)_2C_2O_4$: white=**Ca**.	(*c*) Yellow flame =**Na**. Confirm K by $PtCl_4$ and S.V.R. Test for NH_4 by boiling O with KHO & smelling.

As Mn may sometimes precipitate through the solution absorbing oxygen, it is always advisable to filter out a little of this precipitate and fuse it with KHO and KNO_3:—green residue=**Mn**.

TABLE FOR THE SEPARATION OF METALS INTO GROUPS.

Add a drop of HCl and if it produce a precipitate, add excess (*Note* 1).

The precipitate, which may contain
$PbCl_2$
Hg_2Cl_2
$AgCl$,
is collected on a filter and examined by Table A.

GROUP I.

To the filtrate add H_2S water, and if it produce a discoloration, warm to blood-heat and pass H_2S in excess.

The precipitate is to be carefully washed with boiling H_2O till quite free from HCl (*Note* 2). It is then to be washed into a test-tube about half-full of H_2O, and from 10 to 20 drops of NH_4HS having been added, the whole is warmed for a time and filtered (*Note* 5).

(*a*) Insoluble portion, including possibly
HgS
PbS
Bi_2S_3
CuS
CdS,
is examined by Table B.

(*b*) Soluble portion, containing possibly
As_2S_3
Sb_2S_3
SnS
SnS_2
Au_2S_3
PtS_2,
is examined by Table C.

GROUP II.

Evaporate filtrate to dryness in a platinum capsule, and heat till any organic matter present is decomposed. Moisten the residue with strong HCl, and then add H_2O and boil (any insoluble (*Note* 3) if white SiO_2). Take a little of the solution, add HNO_3 and $(NH_4)_2MoO_4$ and boil. If Phosphates be present, a yellow precipitate will be produced (*Note* 4). Take now the rest of the solution, warm it with a drop or two of HNO_3 and then add NH_4Cl and NH_4HO, the latter in slight but distinct excess; boil and filter (*a*). Add to the filtrate NH_4HS in excess, boil and filter (*b*).

(*a*) NH_4HO
Precipitate may (in absence of PO_4) contain
Fe_26HO
Cr_26HO
Al_26HO
$Ce2HO$
Wash with boiling H_2O and examine by Table D.
(In presence of PO_4)
It may contain
$FePO_4$
$AlPO_4$
$CrPO_4$
Ce_32PO_4
Ba_32PO_4
Sr_32PO_4
Ca_32PO_4
Mn_32PO_4
Mg_32PO_4
Wash with boiling water and examine by Table E.

Division (a).

(*b*) NH_4HS
Precipitate may contain
MnS
ZnS
NiS
CoS
Wash with H_2O containing NH_4HS and examined by Table F.

Division (b).

GROUP III.

Add to filtrate $(NH_4)_2CO_3$ and boil.

Precipitate may contain
$BaCO_3$
$SrCO_3$
$CaCO_3$
examined by Table G.

GROUP IV.

Filtrate may contain
Mg
Li
K
Na
examined by Table II.

GROUP V.

NOTES.

(1) Too much excess HCl prevents the rapid precipitation of Cd by H_2S.

(2) Known by testing washings with $AgNO_3$ and continuing to wash and test till no precipitate is produced.

(3) Cerium leaves a very dark red residue only soluble in strong acid.

(4) A little patience here, as in dilute solutions the precipitate does not form instantly.

(5) When Cu is suspected from the Preliminary Examination, take care not to use yellow NH_4HS as it always dissolves some CuS.

TABLE A.

SEPARATION OF METALS OF GROUP I.

After washing the precipitate once with cold water; put the funnel over a fresh tube and pour on some boiling water.

<table>
<tr>
<td rowspan="2">The filtrate may contain
PbCl
Test while still hot with K_2CrO_4
Yellow Precipitate = Pb.</td>
<td colspan="2">Any precipitate remaining on the filter is washed with boiling water till all trace of Pb is removed, and then percolated with dilute NH_4HO (1 in 3).</td>
</tr>
<tr>
<td>Any black precipitate which remains on the filter is NH_2Hg_2Cl, and proves the presence of Hg_2.</td>
<td>The filtrate is diluted with an equal bulk of water, and then cautiously acidulated with HNO_3 (to re-precipitate AgCl previously dissolved by the NH_4HO).
White precipitate = Ag.</td>
</tr>
</table>

NOTE.—Instead of filtering, the whole of this analysis may be done by decantation, as the precipitates are heavy and settle rapidly.

TABLE B.

SEPARATION OF METALS OF GROUP II., DIVISION (a).

Wash precipitate with boiling water, and then transfer it to a small porcelain dish, add a few drops of HNO_3, and warm till red fumes cease, and repeat this heating with HNO_3 till an additional drop fails to cause any more red fumes. Now wash the contents of the basin into a tube with a little water (1), add H_2SO_4 till no more precipitate forms, then cool and add an equal bulk of spirit of wine (methylated).

Any **Precipitate** may contain HgS (2), and $PbSO_4$. Percolate with a strong solution of $NH_4C_2H_3O_2$, and test filtrate with K_2CrO_4. Yellow = Pb. Any black residue now remaining in the filter will be HgS, and is to be confirmed by dissolving in HCl by the aid of a crystal of $KClO_3$, and (after boiling free from Cl) adding $SnCl_2$, and boiling. Grey precipitate = Hg.	To the **Filtrate**, which may still contain Bi, Cu, and Cd, add NH_4HO in excess.	
	Any **Precipitate** will be Bi3HO, and is to be confirmed by dissolving in the least possible quantity of HCl by the aid of heat, and pouring into H_2O. White – Bi.	The **Filtrate**, if blue in colour, contains Cu for certain, and possibly also Cd. If not blue, no Cu is present, and Cd is to be directly tested for by adding NH_4HS. Yellow = Cd. If Cu be present, then add KCy until the blue colour is discharged, and pass H_2S, when any Cd will be precipitated as yellow CdS.

NOTE 1.—Too much water added might precipitate any Bi, as Oxy-Nitrate.

2.—If any Cl have been left in the original group precipitate (through inefficient washing) the HgS will dissolve and be lost.

TABLE C.

SEPARATION OF METALS OF GROUP II., DIVISION (b).

First Method, in Absence of Gold and Platinum.

Acidulate with HCl to cause the reprecipitation of the sulphides. If a decided yellow, orange, or black precipitate separates, then proceed to filter out; but if only a cloud of precipitated sulphur forms (not separating readily, and nearly white in colour), no metals of this division are present. After washing the sulphides, suspend them in a cold solution of the B.P. ammonium carbonate, shake up for a few minutes, and filter.

<table>
<tr>
<td rowspan="4">The filtrate may contain $(NH_4)_3AsS_4$. Add HCl in excess, and if present As will be reprecipitated as yellow As_2S_5. Filter out and confirm by drying and heating with KCy and Na_2CO_3 in a small tube, thus getting a mirror of metallic arsenic, or, if preferred, by Fleitman's test.</td>
<td colspan="3">Any orange or yellow precipitate still remaining may be sulphides of Sb or $Sn^{(ic)}$. Dissolve in strong boiling HCl, dilute a little, and put into a platinum dish with a rod of zinc so held that it dips in the fluid and touches the platinum outside the liquid. Electrolysis will set in and cause the Sb to deposit as a black stain closely adhering to the platinum, while Sn will deposit as loose metallic granules. Boil with HCl (after washing) and the Sn will dissolve, forming $SnCl_2$ and giving a precipitate with $HgCl_2$; while the Sb will remain undissolved, and may be confirmed by oxidizing with a drop of HNO_3, then dissolving in solution of $H_2C_4H_4O_6$ and getting the characteristic precipitate with H_2S.</td>
</tr>
<tr>
<td colspan="3">Second Method in Presence of Gold and Platinum.
When the precipitate from the NH_4HS by dilute HCl is dark in colour, either $Sn^{(ous)}$ Au or Pt must be present. In this case the separation had better be conducted as follows. Boil the mixed sulphides at once with strong HCl as long as H_2S is given off; dilute slightly, and filter.</td>
</tr>
<tr>
<td rowspan="2">Filtrate may contain $SbCl_3$ and $SnCl_2$, which are separated by electrolytic process above described.</td>
<td colspan="2">Precipitate may contain As_2S_3, Au_2S_3, and PtS_2. If it be yellow, simply confirm the As by fusion in a tube as above; but if it be blackish, then Au or Pt are certainly present. In this case digest the precipitate with solution of ammonium carbonate as above.</td>
</tr>
<tr>
<td>Filtrate may contain $(NH_4)_3AsS_3$. Reprecipitate with HCl, and prove by fusion as above.</td>
<td>Precipitate may be Au_2S_3 and PtS_2. Dissolve in aqua regia; dilute, and test a portion for Au with $SnCl_2$ (Purple = Au), and another for Pt by KCl and S.V.R. Yellow = Pt.</td>
</tr>
</table>

TABLE D.

SEPARATION OF METALS OF GROUP III., DIVISION (a).

(*Note* 1.) Wash and transfer to a platinum or silver dish, and fuse with $KNaCO_3$ and KNO_3. Boil the residue in water and filter.

<table>
<tr><td rowspan="2">Insoluble portion may contain Fe and Ce. (Note 2.) Moisten with strong HCl, and then add H_2O and boil. Test a portion of the solution for Fe by K_4FeCy_6 Blue = Fe. To remainder add citric acid, and then excess of NH_4HO, and finally $(NH_4)_2C_2O_4$. White = Ce.</td><td colspan="2">The solution (which if yellow contains Cr) is mixed with Na_2HPO_4 acidulated with $HC_2H_3O_2$ and boiled.</td></tr>
<tr><td>Precipitate is $AlPO_4$. Gelatinous white = Al.</td><td>Filtrate treated with $AgNO_3$ gives a red, or with $BaCl_2$ a yellow if Cr be present (Note 3).</td></tr>
</table>

NOTES.

1. If this group precipitate be deep reddish-brown, nothing is probably present but Fe. If it be at all greenish, **Cr is present.** If it be white or pale red, take a little on a watch-glass, and touch it with an excess of KHO and observe effect.
   Originally white and soluble, only Al.
   " " insoluble " Ce.
   " pale red, and becoming deep red, and partly dissolving, Fe and Al both present (probably).
   " " " not darkened by KHO, but darkened by NaClO, Fe and Ce both present.
2. If Ce be present, the red residue is with great difficulty soluble, even in strong HCl.
3. Sometimes the NH_4HO brings down Mn along with the Fe in this group; and both the residue and solution being then bright green, the yellow of the Cr is of course masked. In this case boil the filtrate with HCl and S.V.R., when the green of the manganate will be removed, while the chromate will be reduced to Cr_2Cl_6 and turned greenish. If therefore the originally green solution be entirely decoloured by HCl and S.V.R. nothing but Mn was present; but if a green tint remain, then Cr was also present. This is of rare occurrence, but must always be kept in view when the original fusion gives a green residue.

TABLE F.

SEPARATION OF METALS OF GROUP III. (DIVISION a) IN PRESENCE OF PHOSPHORIC ACID.

(*Note* 1.) Dissolve precipitate in dilute HCl, add excess of Na_2HPO_4 and then excess of $NH_4C_2H_3O_2$ and boil.

<table>
<tr>
<td colspan="2">Precipitate may be (Note 2) $FePO_4$, $AlPO_4$, Ce_32PO_4 wash with boiling H_2O and percolate with some boiling dilute KHO.</td>
<td colspan="4">Filtrate, if green in colour, contains Cr. (but if perfectly colourless, that metal may be noted as absent). Add K_2CrO_4 and warm.</td>
</tr>
<tr>
<td rowspan="3">Residue may contain Fe and Ce
Dissolve in HCl and test a portion for Fe by K_4FeCy_6. Blue = Fe.
To the remainder add citric acid and then NH_4HO in excess. An immediate white or a white after adding $(NH_4)_2C_2O_4$ = Ce.</td>
<td rowspan="3">Filtrate may contain $AlPO_4$ supersaturate with $HC_2H_3O_2$. Whitegelatinous = Al.</td>
<td rowspan="3">Precipitate $BaCrO_4$. Yellow = Ba.</td>
<td colspan="3">Filtrate must be tested for Sr by flame test (If present, Note 3), if absent, proceed as follows. Add $(NH_4)_2C_2O_4$.</td>
</tr>
<tr>
<td rowspan="2">Precipitate is CaC_2O_4. White = Ca.</td>
<td colspan="2">Filtrate is mixed with a little $H_3C_6H_5O_7$ cooled and excess of NH_4HO added (Note 4).</td>
</tr>
<tr>
<td>Precipitate may contain Mn_32PO_4 or Mg_32PO_4 (See Note 5).
Separation, if necessary, by dissolving in dilute HCl, adding excess of $NH_4C_2H_3O_2$, boiling, and dropping in Fe_2Cl_6 till a reddish tint is produced. Filter out the $FePO_4$ thus produced, and to the filtrate add NH_4Cl, NH_4HO, and NH_4HS, to remove Mn and Fe. Again filter, concentrate to a small bulk, and test when quite cold for Mg by NH_4HO and Na_2HPO_4.</td>
<td>Filtrate may contain Cr only, prove by fusion if necessary.</td>
</tr>
</table>

NOTES.

1. This precipitate, if free from Ce, Cr, and Mn, is much more simply worked. Therefore take a little before dissolving and put it on a porcelain crucible-lid with a few drops of strong KHO and a crystal of KNO_3 evaporate to dryness and fuse. If no bright yellow or green residue be formed Cr and Mn are respectively absent. Take another portion of the group precipitate on a white porcelain lid, and add some solution of chlorinated soda or lime; if it does not turn yellow, then Ce is absent (if Mn be present this last test will turn the precipitate brown) so that it is only when it does not change colour at all that the positive absence of Ce can be insured.
2. Here $CrPO_4$ should be found, as it is theoretically insoluble in acetic acid; but in practice it is, when freshly precipitated, nearly entirely soluble, and passes on as shown in the Table. If its presence is suspected, a little of the precipitate may be fused as above.
3. If Sr be present (known by its crimson flame, and distinguished from the mere orange-red of Ca) it must be removed by adding a little very dilute H_2SO_4, letting stand for twenty minutes in a warm place, and then filtering out the $SrSO_4$ formed. In this case excess of ammonium acetate must be added before proceeding to test for Ca.
4. If no Cr is present the citric acid need not be used, as it is only added to prevent the precipitation of $CrPO_4$ by the NH_4HO.
5. If no Mn was found by the preliminary fusion (*Note* 1) this precipitate is all Mg; but if Mn be present it must be first removed before Mg can be definitely proved.

TABLE F.

SEPARATION OF METALS OF GROUP III., DIVISION (b).

CASE I.—If the group precipitate be white or flesh-coloured, nothing is present but MnS and ZnS; and it then only remains to dissolve in dilute HCl, add NaHO in excess, boil, and filter.

The **filtrate** may contain **Zn** dissolved in excess of NaHO; add excess of $HC_2H_3O_2$ and then K_4FeCy_6. White = Zn.	Any **precipitate** may be Mn2HO, which must be confirmed by fusion on platinum foil with $KNaCO_3$ and KNO_3. Green residue = Mn. (*Note.*) The supposed precipitate of Mn must be confirmed, because any trace of Fe escaping precipitation in its own group might appear here as Mn.

CASE II.—If the group precipitate be dark in colour, then Co and Ni may also be present. In this case a black residue of NiS and CoS will remain insoluble in the diluted HCl. Any such residue must be filtered out and dissolved in strong boiling HCl, or Aqua Regia, if necessary; then add excess of KCy, and boil in the fume chamber, adding more HCl if necessary, until all further smell of HCy ceases to be developed. Then add KHO in excess.

Any **precipitate** contains Ni; confirm by drying and heating in borax bead.	The **filtrate** may contain Co; confirm by evaporating to dryness, and heating **residue** in borax bead.

SEPARATION OF METALS OF GROUP IV.

<table>
<tr><td colspan="3">Dissolve the precipitate in $HC_2H_3O_2$ and add K_2CrO_4 in excess.</td></tr>
<tr><td rowspan="2">Any precipitate is $BaCrO_4$. Yellow = Ba.</td><td colspan="2">Take a small portion of the filtrate and add some saturated solution of calcium sulphate, warming gently. If no precipitate should form, Ca only is present, and may be confirmed at once by adding $(NH_4)_2C_2O_4$ to the remainder of the filtrate. But if a precipitate be produced Sr is present, and must be separated by adding a few drops of very dilute H_2SO to the said remainder, and letting the whole stand in a warm place for fifteen or twenty minutes.</td></tr>
<tr><td>Any precipitate is $SrSO_4$; confirmed by being perfectly insoluble after digestion for some time at a gentle heat with a strong solution of $(NH_4)_2SO_4$ and a little NH_4HO (to remove any $CaSO_4$ accidentally precipitated). White residue giving crimson flame = Sr.</td><td>The filtrate may contain Ca, confirmed by adding NH_4HO and $(NH_4)_2C_2O_4$. White = Ca.
(Note.) To ensure that Sr is fully separated, see that a portion of this filtrate gives no precipitate by warming with a saturated solution of Ca SO_4.</td></tr>
</table>

TABLE H.

SEPARATION OF METALS OF GROUP V.

Divide the solution into $\frac{1}{3}$ and $\frac{2}{3}$. Take the $\frac{1}{3}$ portion, and concentrate by evaporation if very dilute, cool perfectly, and add excess of NH_4HO and Na_2HPO_4. White = **Mg**. Evaporate the filtrate to dryness on the water bath, and take up with *boiling water*, when any white insoluble residue is **Li**, provided it gives a crimson flame on a platinum wire previously dipped in HCl.

Take the remaining $\frac{2}{3}$ and evaporate to dryness, and heat till all fumes of ammonium salts cease to be evolved. Take up the residue with the smallest quantity of boiling water (pouring off from and disregarding any insoluble matter). Then acidulate with HCl, dip in a wire and test flame, looking first at it with the naked eye, and then through a piece of blue glass (to cut off the sodium yellow).

Red	Li (disregard if already found in the $\frac{1}{3}$ portion).
Yellow	Na.
Violet	K.

Confirm K by adding $PtCl_4$ to the rest of the acidulated solution, and getting when cold a yellow precipitate of $PtCl_4 2KCl$.

Test for NH_4 by boiling some of the original solution with KHO, and getting off NH_3.

Having thus ascertained the metals present in the substance under examination, it is now necessary to turn our attention to the examination for acidulous radicals. This is a matter of some nicety, as it is impossible to construct tables for the separation of acidulous radicals so simple and direct as those already considered for metals. Much depends, even with the latter, on continued practice in the laboratory, so that though the tyro may fall into errors, he will soon learn to steer clear of the numerous rocks ahead which are invariably met with. It frequently occurs that two or more substances are mixed together which so completely decompose each other as to render the elucidation of the problem entirely a matter of experience. Let the student therefore seek to thoroughly grasp the *reasons* for the steps he takes, and when he has done so (but not before) let him acquire the habit of thinking for himself, rather than slavishly following any set system to the exclusion of the use of his own brains and experience.

IV. PRELIMINARY EXAMINATION FOR ACIDULOUS RADICALS.

The presence of soluble hydrates or carbonates, and also of organic acids generally, has been already provisionally proved or otherwise in the general preliminary examination. There is really only one step of preliminary investigation for acids which gives striking results in some few instances; therefore, following the system already adopted in the case of bases, it is simply the easily recognisable indications which will be here given.

Treat a little of the solution or substance with an excess of strong H_2SO_4, and if no action be apparent, heat gently, observe, and smell.

Effect Noticed.	Radicals Inferred.	Confirmation.
Immediate effervescence, no smell	Carbonates	Pass gas evolved into Ca2HO solution, and get a white precipitate.
No effervescence in cold, but on heating effervescence without smell	Oxalates	Use acid course, Group III., after properly preparing solution.
Smell of H_2S	Sulphides	Hold over the tube a piece of paper moistened with $Pb2C_2H_3O_2$ and observe black stain.
Smell of H_2S and deposit of S_2	Polysulphides	Same proof with lead paper, the distinction being deposit of sulphur.
Smell of SO_2	Sulphites	Place some of the solution in a tube with HCl, and hold a piece of lead paper over the mouth, getting no stain, then add a fragment of Zn and warm, and get a stain.
Smell of SO_2 and deposit of S_2	Hyposulphites	1. Prepare some AgCl and digest a little of it in some of the solution, when it should dissolve. 2. Make a little very dilute solution of iodine and add to it a little of the hyposulphite solution, when it will be bleached.
Deep brown colour, and violet fumes on heating	Iodides or Iodates	Add starch paste and HNO_3 or chlorine water, and get a blue colour. For distinction see Iodates.
Deep reddish colour, and red fumes on heating	Bromides or Bromates	Add starch paste and HNO_3 or chlorine water, and get a golden colour. For distinction see Bromates.
Smell of HCN	Cyanides	Hold a crucible lid over the tube, moistened with a drop of NH_4HS. When it has absorbed the fumes, add a drop of NH_4HO and evaporate at a very gentle heat (under 212°). When dry, add to the residue a drop of Fe_2Cl_6, and get a blood-red stain, not discharged by dilute HCl but bleached by $HgCl_2$.

Smell of HCN and crystalline deposit	Ferrocyanides or Ferricyanides	Test original (1) with a fresh solution of $FeSO_4$ and (2) with Fe_2Cl_6. Blue with both = Ferrocyanide. ,, ,, $FeSO_4$ only = Ferricyanide.
Smell of HCN and deposit of S_2	Sulphocyanides	Test original with Fe_2Cl_6 and get a blood-red colour, not discharged by dilute HCl but bleached by $HgCl_2$.
Smell of vinegar	Acetates	Heat original with S.V.R. and H_2SO_4 and get off acetic ether. (Apple-like odour.)
Rapid blackening and smell of burnt sugar	Tartrates	Confirmed in Group IV. of the Acid Course after proper preparation of the solution.
Slow blackening and smell of burnt sugar, but slightly more acetous	Citrates	Confirmed in Group IV. of the Acid Course after proper preparation of the solution.
Smell like chlorine	Hypochlorites or Chlorates	Treat a portion of the original with KI, starch paste, and acetic acid; if a blue be produced, it is a hypochlorite. If not, then take a second portion and test with $AgNO_3$ and get no precipitate. Then evaporate a third portion of original to dryness, and having heated the residue to drive off all the oxygen, dissolve it in water and get white precipitate with $AgNO_3$.
Red fumes, without any blackening of solution	Nitrites	Confirm by mixing solution of KI with starch paste and acidulating with HCl. This mixture ought to remain quite white; but on adding a drop or two of a nitrite in solution a blue will be developed.
White fumes, not altering when a fragment of Cu is dropped in	Chlorides	Original gives a curdy-white precipitate with HNO_3 and $AgNO_3$, instantly soluble in NH_4HO but insoluble in strong boiling HNO_3.
White fumes, turning orange-red when a fragment of Cu is dropped in	Nitrates	Original mixed with a fresh solution of $FeSO_4$ and then H_2SO_4 poured down to the bottom of the tube, gives a black ring where the fluids meet.
Characteristic smells, with tendency to darken	Benzoates, Succinates, Valerianates, Carbolates, Sulphocarbolates, Sulphovinates	Confirm by Acid Course, Group V.

V. PREPARATION OF THE SOLUTION BEFORE PROCEEDING TO THE ANALYSIS OF ACIDULOUS RADICALS.

Case I. THE SUBSTANCE IS SOLUBLE IN WATER, OR HAS BEEN GIVEN IN SOLUTION.

1. If any metals other than alkalies have been found, add strong solution of Na_2CO_3 till the whole is just distinctly alkaline, boil and filter any precipitate which forms. By this means the heavy metals are removed, and the acid radicals, being transferred into sodium salts, are then in a proper state for analysis.

2. Divide the solution thus obtained into six parts.
   (*a*) One part to be acidulated with HCl, and kept for Step 1.
   (*b*) Another part to be acidulated with HNO_3, and kept for Step 2.
   (*c*) Another part to be acidulated with $HC_2H_3O_2$, and kept for Step 3.
   (*d*) Another part to be rendered just acid with HCl, and then just alkaline with NH_4HO, and kept for Step 4.
   (*e*) Another part to be made exactly neutral by boiling and dropping in *very dilute* HNO_3. If by mistake too much HNO_3 be put in we must then work back again with *very dilute* NaHO till *just neutral*. This part to be saved for Step 5.
   (*f*) The last part to be kept against contingencies.

Case II. THE SUBSTANCE IS INSOLUBLE IN WATER, BUT SOLUBLE IN ACIDS.

1. Boil a little of the solid with strong solution of NaHO for some time, then dilute and filter, rejecting the precipitate, and using only the filtrate.
2. Divide the filtrate into six parts, and treat as above directed.

Case III. THE SUBSTANCE IS INSOLUBLE IN WATER AND ALL ACIDS.

In this case a fusion will have already been performed, for the metal and the acid must be got from the portion of the residue after fusion which was soluble in water.

VI. COURSE FOR THE DETECTION AND SEPARATION OF ACIDULOUS RADICALS.

Step 1. Use the portion (*a*) of the prepared solution, acidulated with HCl.

A. To a part of (*a*) add $BaCl_2$. White precipitate, insoluble on dilution with H_2O and boiling, and also insoluble in boiling HNO_3 = **Sulphate.**

B. To another portion of (*a*) add Fe_2Cl_6.
  1. A deep blue precipitate turned reddish-brown by KHO and blue restored by HCl = **Ferrocyanide.**
  2. A blood-red precipitate bleached by $HgCl_2$ = **Sulphocyanide.**
  3. " " not bleached by $HgCl_2$ = **Meconate.**

C. To another part of (*a*) add $FeSO_4$. A deep blue precipitate the colour of which is destroyed by KHO and restored by HCl = **Ferricyanide.**

2. Use the portion (*b*) of the prepared solution, acidulated with HNO_3, and disregard any precipitate which does not subside readily in a curdy form on boiling and shaking.

To a part of the solution add a drop of $AgNO_3$, and, if it produce a precipitate, add excess, warm, and shake well.

1. A *curdy-white* precipitate, soluble in strong HNO_3 (boiling), and also in NH_4HO = **Cyanide** (confirm by Iron test).
2. A *curdy-white* precipitate insoluble in strong boiling HNO_3, but instantly soluble in NH_4HO = **Chloride.**
3. A *curdy, dirty*, or *yellowish-white* precipitate, slowly soluble in NH_4HO = **Bromide** (confirm by chlorine water and chloroform).
4. A *curdy-yellow precipitate* insoluble in and turned white by NH_4HO = **Iodide** (confirm by chlorine water and starch paste).

SEPARATIONS.

A. To distinguish between argentic cyanide and chloride, filter off the precipitate, wash well with boiling water, remove from the filter, and heat to redness in a porcelain crucible. Digest the fused residue in heated HNO_3, which will dissolve the Ag left by the decomposition of the AgCy, but will leave the AgCl, if any, untouched as a white residue. The HNO_3 will evolve red fumes when dissolving the Ag, and the solution will give a white precipitate with HCl, thus proving the metallic silver, and therefore by inference also the presence of the decomposable cyanide. If the precipitate be all AgCl, it will simply fuse to a horny mass perfectly unaffected by HNO_3.

B. To **detect AgCl in the presence of AgI.** Wash the precipitate well by decantation, and then add some dilute NH_4HO (B.P. liquor 1 in 3), shake up and filter (any AgI remains insoluble). Dilute the filtrate, and add a slight excess of HNO_3, and if any AgCl was present, it will separate again as a pure white curdy precipitate.

C. To **detect AgCl in the presence of AgBr.** Remove any AgI, if necessary, by digestion with NH_4HO. Filter and reprecipitate with HNO_3, then boil the washed precipitate with strong KHO, dilute and filter. Evaporate the filtrate to dryness, and distil the residue with $K_2Cr_2O_7$ and H_2SO_4. If Cl be present, deep red fumes of chlorochromic acid will be formed, which will, when received into very dilute NH_4HO, colour it yellow.

Note 1.—In practice the use of the separations must be governed by what is found previously. For example, if no HCy was given off in the preliminary heating with H_2SO_4, the ignition of this group need not be resorted to. Again, if, say, neither Cy or Br were found in the preliminary step, of course any silver precipitate soluble in NH_4HO must be only AgCl. The best way, if I be found in the preliminary course, is at once to test also for Br, by taking a small portion of the original, adding a drop of starch paste, and then chlorine water *until the blue of the iodine is entirely bleached*. If now some chloroform be added and the whole shaken, any Br present will colour the chloroform golden red. It is only in the event of Br being distinctly found in the preliminary (or as just advised) that the distillation of a chloride need be resorted to, and even then only when the silver precipitate looks whiter than AgBr ought to be, and is in part instantly soluble in NH_4HO.

Note 2.—A very good rough way of getting at the possible presence of a chloride when a bromide has already been found, is to take some of the solution and add carefully dilute $AgNO_3$ till only a part of the whole is precipitated, then to filter off, and to once more add $AgNO_3$ to the filtrate, this time in excess, and again filter. Compare the colour of the two precipitates, and if both are alike then it is all AgBr, but if the latter portion be whiter than the first, then AgCl is also present. This depends on the fact that the Ag combines first with any Br present, and only forms the white AgCl after the AgBr has ceased to be precipitated. The separation of AgI and AgCl is so simple that it should always be done if I can be found.

Step 3. Use the prepared solution (*c*) acidulated with $H_2C_2H_3O_2$.

A. Bring a part of the solution (*c*) to the boiling point, and drop in $CaCl_2$. A white precipitate instantly soluble in HCl = **Oxalate.**

B. Bring another part of the solution (*c*) to the boil, and drop in Fe_2Cl_6, avoiding excess. White precipitate soluble in HCl = **Phosphate,** or **Arseniate.**

Distinguish by adding $AgNO_3$ to a little of the exactly neutralized prepared solution :—

1. Yellow soluble in NH_4HO, and also in HNO_3 = **Phosphate.**
2. Red ,, ,, ,, ,, = **Arseniate.**

C. To a third part of the solution (*c*) add $Pb2C_2H_3O_2$. Yellow = **Chromate.**

Note 3.—(This test need not be applied unless the original solution was distinctly yellow or orange.) If found, the original solution should be tested for *chromate* and *bichromate* by acids and alkalies which change their respective colours from yellow to orange and *vice versâ*.

Step 4. Use the portion of the solution (*d*) which was neutralized by HCl and then rendered faintly alkaline with NH_4HO; but do not take this step at all unless the substance was distinctly blackened by heat during the preliminary examination, or unless the presence of boracic acid has been made probable by the flame test.

A. To a portion of the solution (*d*) perfectly cold add $CaCl_2$ in excess, shake well, and let stand for a short time.

1. The original was blackened. If no oxalate has been found, and a crystalline white precipitate *entirely soluble* after washing in cold KHO is formed = **Tartrates.**

   If an oxalate has been already found, collect the precipitate on a filter, wash well with cold water, and percolate with cold KHO. Any calcium tartrate present *will dissolve* and *reprecipitate on boiling*.
2. **A gelatinous white** insoluble in cold KHO = possibly **Borates.** (Confirm by turmeric test, but otherwise disregard it, as phosphates and arseniates may equally precipitate here.)

B. To the filtrate from (*a*) (or, if no tartrate has been found, to the same solution) add another drop or two of NH_4HO, and boil slowly for some time. A white precipitate = **Citrate.**

(This precipitate should be *insoluble* after washing in KHO).

Step 5. ʹUse portions of the prepared solution (*e*) which was exactly neutralized.

A. Add Fe_2Cl_6 (1) Blue precipitates *disregard, already found.*

(2) Black, or bluish black = **Tannate** or **Gallate.**

(*a*) Add to the original solution KHO, Green gradually becoming brown = **Gallate.** Rapidly becoming brown = **Tannate.** (Also apply gelatin separation.)

(3) Red colour, discharged by HCl = **Acetates** or **Pyrogallates.**

(*b*) Add KHO to original solution, **Acetates,** no colour; **Pyrogallates,** black.

(Other reds not discharged by HCl to be disregarded.)

(4) Violet colour = **Carbolate, Sulphocarbelate, alicylate.**

(Former two have given smell of carbolic acid in preliminary examination, and the latter not). The **Sulphocarbolate** on ignition will leave a sulphate, thus distinguishing it from carbolate.

(5) Pinkish precipitates = **Succinates** and **Benzoates.** Distinguished by digestion with NH_4HO, filtration, concentration of filtrate and supersaturation with HCl; when **Benzoic Acid** precipitates in fine feathery crystals; while **Succinic Acid** remains in solution.

Step 6. Test for a Nitrate (if not already found in the preliminary course) by adding $FeSO_4$ and strong H_2SO_4 and getting a black ring.

If an iodide has been previously found, it must first be separated by digesting the solution with **Argentic Sulphate** and filtering before testing for the nitrate.

A rougher method is to introduce some starch paste and to acidulate with HCl and finally drop in some sodium sulphite, which reduces the nitric to nitrous acid; and this latter, acting on the iodide, will liberate iodine, causing a blue if any nitrate be present in the solution.

VII. SOLUBILITY.

An important consideration before proceeding to the Acidulous Course.

Looking to the metals found, the question arises, what acidulous radicals could possibly be there, supposing the original substance to be soluble or insoluble in water or acids, or totally insoluble. Of the solubility of the commoner salts, the following table will show this, and a careful study of it will save much unnecessary and often misleading testing for acids. **The usual radicals are in words and the rarer ones in symbols bracketed.**

Metals found.	If soluble in water, test for the following radicals.	If insoluble in water but soluble in acids, test for the following radicals.	If insoluble in acids, fuse with K, $NaCO_3$, extract with H_2O, and test the solution for the following radicals.
Silver	Nitrate, Nitrite, Sulphate, Acetate (ClO, ClO_3, BrO_3, S_2O_3)	Oxide, Sulphide, Carbonate, Phosphate, Cyanide, Oxalate, Tartrate, Citrate (AsO_4, CrO_4, IO_3, S_2O_3)	Chloride, Iodide, Bromide
Mercury (ous)	Nitrate, Acetate, Sulphate (ClO, ClO_3, IO_3, BrO_3, NO_2, BO_3, $C_4H_4O_6$)	Oxide, Sulphide, Chloride, Iodide, Oxysulphate (PO_4, AsO_4, C_2O_4, CrO_4, $C_4H_4O_6$, $C_6H_8O_7$)	Chloride, Iodide, Bromide
Mercury (ic)	Chloride, Nitrate, Sulphate, Acetate (ClO, ClO_3, IO_3, BrO_3, Cy, S_2O_3, CrO_4, NO_3)	Oxide, Sulphide, Iodide, Carbonate, Oxysulphate (PO_4, C_2O_4, AsO_4, CrO_4, $C_4H_4O_6$)	Sulphide, Iodide
Lead	Acetate, Nitrate (Cl, I, ClO, ClO_3, BrO_3, NO_2, $C_6H_5O_7$)	Oxide, Sulphide, Carbonate, Phosphate, Oxalate (Cl, I, Cy, SO_3, S_2O_8, IO_3, BrO_3, AsO_4, CrO_4, $C_4H_4O_6$)	Sulphate, Chromate, Chloride, Iodide
Bismuth	Nitrate, Chloride, Sulphate, Acetate (Br, IO_3, BrO_3, ClO, ClO_3, $S\ O_3$, NO_2, $C_6H_5O_7$)	Oxynitrate, Oxychloride, Oxysulphate, Oxide, Sulphide, Carbonate, Phosphate (CrO_4, AsO_4, BO_3, C_2O_4, I, SO_4, $C_4H_4O_6$)	None
Copper (ic)	Chloride, Nitrate, Sulphate, Acetate (NO_2ClO_3, S_2O_3, CrO_4, ClO, Br, IO_3, BrO_3, I, $C_4H_4O_6$, $C_6H_5O_7$)	Oxide, Sulphide, Carbonate, Phosphate, Arsenite, Oxyacetate (AsO_4, BO_3, Cy, SO_3)	,,
Copper (ous)	Sulphate (Cl, Br)	Iodide (Cl, Br)	,,
Cadmium	Chloride, Nitrate, Iodide, Sulphate (ClO, ClO_3, Br, IO_3, BrO_3, SO_3, S_2O_3, NO_2, $C_2H_3O_2$, $C_4H_4O_6$, $C_6H_5O_7$, BO_3)	Oxide, Sulphide, Carbonate, Phosphate (BO_3, C_2O_4, $C_4H_4O_6$)	,,
Antimony	Chloride, Tartrate ($C_2H_3O_2$, C_2O_4)	Oxide, Sulphide, Oxichloride (SO_4, PO_4, CrO_4, I)	,,
Tin (Stannous)	Chloride, Sulphate (ClO, ClO_3, Br, NO_2, NO_3, S_2O_3, $C_2H_3O_2$, $C_4H_4O_6$)	Oxide, Sulphide, Phosphate, Chromate (BO_3, C_2O_4)	,,

Tin (Stannic)	Chloride (ClO_3, $C_2H_3O_2$, C_2O_4)	Oxide, Sulphide (SO_3)	None
Gold	Chloride	Sulphide (Cy)	,,
Platinum	Chloride	Sulphide	,,
Iron (Ferrous)	Chloride, Sulphate, Iodide (see ferric, also SO_3, S_2O_3)	Oxide, Sulphide, Carbonate, Phosphate, Arseniate (C_2O_4, BO_3, CrO_4, Cy, $C_4H_4O_6$, AsO_3)	,,
Iron (Ferric)	Chloride, Nitrate, Sulphate, Acetate (Br, IO_3, BrO_3, ClO_3, NO_2, CrO_4, $C_4H_4O_6$)	Oxide, Sulphide, Iodide, Phosphate, Arseniate (C_2O_4 (when dried), BO_3, and SO_4, when basic)	,,
Aluminium	Like Iron	Like Iron	,,
Cerium	Chloride	Oxide and Oxalate	Oxide
Chromium	Chloride, Sulphate, Acetate, Nitrate (Br, ClO, ClO_3, IO_3, BrO_3, S_2O_3, SO_3, C_2O_4, $C_4H_4O_6$, $C_6H_5O_7$)	Oxide, Phosphate, Arseniate (BO_3, CrO_4, [illegible])	Oxide
Manganese	Chloride, Sulphate, Acetate, Nitrate (Br, ClO, ClO_3, IO_3, BrO_3, SO_3, S_2O_3, NO_2, CrO_4)	Oxide, Sulphide, Carbonate, Phosphate (AsO_4, C_2O_4, BO_3, Cy, $C_4H_4O_6$, $C_6H_5O_7$)	None
Zinc	Chloride, Sulphate, Acetate, Nitrate (ClO, ClO_3, Br, IO_3, BrO_3, NO_2, S_2O_3, SO_3, CrO_4, $C_6H_5O_7$)	Oxide, Sulphide, Carbonate, Phosphate (C_2O_4, BO_3, ASO_4, Cy, $C_4H_4O_6$)	,,
Nickel	Chloride, Nitrate, Sulphate, Acetate (ClO, ClO_3, IO_3, BrO_3, SO_3, S_2O_3, Br, NO_2)	Oxide, Sulphide, Carbonate, Phosphate (AsO_4, BO_3, CrO_4, Cy, $C_4H_4O_6$, $C_6H_5O_7$, C_2O_4)	,,
Cobalt	Chloride, Nitrate, Sulphate, Acetate (ClO, ClO_3, IO_3, BrO_3, SO_3, S_2O_3, Br, NO_2, $C_6H_5O_7$)	Oxide, Sulphide, Carbonate, Phosphate (AsO_4, BO_3, CrO_4, C_2O_4, Cy	,,
Barium	Chloride, Nitrate, Acetate, Oxide (slightly) (ClO, ClO_3, I, Br, IO_3, BrO_3, S_2O_3, NO_2, Cy, $C_6H_5O_7$, S)	Carbonate, Phosphate, Oxalate, Chromate (O, AsO_4, BO_3, SO_3, $C_4H_4O_6$)	Sulphate
Strontium	Like Barium (except $C_6H_5O_7$)	Like Barium	Sulphate
Calcium	Like Barium (except $C_6H_5O_7$ soluble in cold but not in boiling water, $CaSO_4$ also slightly soluble)	Like Barium (except SO_3 which is soluble in H_2O and $CaSO_4$ slightly soluble)	Sulphate
Magnesium	Like Calcium	Like Calcium	None
Lithium	Oxide, Chloride, Sulphate	Carbonate, Phosphate, Oxalate	,,
Potassium	All radicals form soluble salts except those mentioned opposite	$PtCl_4 2KCl$, $KHC_4H_4O_6$, and K_2SiF_6	,,
Sodium	All radicals form soluble salts except	Sodium Antimoniate	,,
Ammonium	Like Potassium		

NOTE.—When a radical is mentioned in more than one column, it means that it is so slightly soluble, as to sometimes appear insoluble at first sight.

CHAPTER VI.

DETECTION OF ALKALOIDS.

1. **Aniline** is a volatile liquid, becoming brownish by exposure, and having a peculiar odour. It is known by the following reactions :—
   1. Heated with solid $HgCl_2$ forms a dark mass, soluble in alcohol to a magenta-coloured solution.
   2. $CaCl_2Ca2ClO$ produces a mauve.
   3. Dissolved in sulphuric acid and submitted to electrolysis, the liquid around the *positive* electrode becomes blue, violet, and finally red.

2. **Conia** (*Conine*) is a volatile liquid with the odour of mice, and is evolved when anything containing it is heated with potassium hydrate. It gives the following reactions :—
   1. HNO_3 gives a blood-red colour.
   2. H_2SO_4 gives a purple followed by an olive-green colour.
   3. Albumen in solution is coagulated.
   4. $AuCl_3$ gives a precipitate; but not $PtCl_4$.

3. **Nicotia** (*Nicotine*) is a volatile liquid having the smell of tobacco. It exhibits the following reactions :—
   1. Albumen in solution is not coagulated.
   2. $AuCl_3$ and $PtCl_4$ both give precipitates.

4. **Quinia** (*Quinine*) is a non-volatile solid, decomposible by heat. It is very slightly soluble in water, but freely in alcohol, ether, and chloroform.
   1. Its solutions are usually fluorescent.
   2. Heated in a dry test-tube, it gives a violet-red sublimate, and an odour of quinoline.
   3. Chlorine water and ammonium hydrate added successively produce a green colour of thalleiochin.
   4. Dissolve the suspected salt in water by the aid of a *slight* excess of dilute sulphuric acid; and add first chlorine water, and then ammonium hydrate, when a bright green colour is produced which is due to the formation of a body called *thalleiochin.*
   5. To a similar acid solution add first chlorine water, then potassium ferrocyanide, and lastly ammonium hydrate, when a red colour is produced which quickly fades.
   6. Strong sulphuric and nitric acids are practically without effect.
   7. Stannic acid, mercuric chloride, and platinic chloride, all cause precipitates in solutions of quinine: the first being yellowish-white, the second white, and the third yellow.

8. When dissolved in hydrochloric acid a white flocculent precipitate is produced on adding sodium hyposulphite. According to Flückiger, the chlorine and ammonia reactions show 1 of quinine in 5000; but if bromine vapour be used instead of chlorine, a perceptible green may be produced in solutions containing $\frac{1}{20000}$ of quinine.

Detection of Cinchonine in Quinine.—*Cinchonine, cinchonidine*, and *quinidine* sulphates are commonly detected in quinine sulphate by Liebig's test as modified by Mr. Stoddart. Take 10 grains of quinine and add to it, in a long, narrow, stoppered bottle, 60 minims of distilled water, acidulated with 10 minims of B.P. dilute sulphuric acid. When quite dissolved, add 40 minims of solution of sodium hydrate (1 part to 12 of water), and then 150 minims of pure ether, with which 3 minims of rectified spirit have been previously mixed. Shake the whole violently for some minutes, and let it stand for twelve hours. At the expiration of that time, examine the line of demarcation between the two liquids with a magnifying glass. Cinchonine will appear as a layer decidedly crystalline, while quinidine will seem like a stratum of fine dust. To the unassisted eye the former shows as a cloud, and the latter as an oily-looking layer.

Students should train their eyes to the practical application of this test.

Detection of Adulterations in Quinine Salts.—Quinine sulphate, being so costly, is liable to many adulterations.

(*a*) *Mineral matters*, such as chalk and calcium sulphate, which are detected by being left on ignition.

(*b*) *Starch and fatty matters* (usually stearine), detected by their insolubility in water acidulated with sulphuric acid.

(*c*) *Common sugar* blackens when a little of the suspected salt is treated with a drop of strong sulphuric acid.

(*d*) *Salicine* reddens under similar circumstances.

(*e*) *Grape* or *starch sugar* (glucose) is detected, with other soluble adulterations, in a solution from which the quinine has been precipitated by barium hydrate, and then the excess of the latter removed by passing carbonic anhydride.

5. **Cinchonia** (*cinchonine*) is a non-volatile solid destructible by heat. It is very slightly soluble in water, but freely in alcohol and chloroform. It is insoluble in ether (distinction from quinia), and gives the following reactions:—

1. Its salts are not fluorescent.
2. Heated in a dry test tube, it behaves like quinia.
3. It yields a precipitate with ammonium hydrate, insoluble when shaken up with ether.
4. Treated with chlorine water and ammonium hydrate, it yields a white deposit instead of a green colour.
5. Shaken up with potassium ferrocyanide, it deposits after a time a yellow precipitate.

6. **Morphia** (*morphine*) is a non volatile solid, destructible by heat. It is soluble in water and alcohol, but not in ether or in chloroform to any extent. It is characterized by the following reactions:—

1. Treated on a watch-glass with a drop of nitric acid, an orange red colour is produced, which is decolorized by stannous chloride or sodium hyposulphite.

2. Treated on a watch-glass with a drop of neutral solution of ferric chloride, an evanescent blue colour is produced. Sulphuric acid should not be present.
3. Moistened with a solution of one part of iodic acid and 15 parts of water, iodine is liberated, which strikes a blue colour with a weak solution of starch. This reaction must not be viewed as conclusive in itself, as several other substances possess the power of liberating iodine. According to Dr. Dupré, if a stratum of very dilute ammonium hydrate be carefully poured upon the mixture, a distinct brown ring will be produced at the point of contact between the two solutions, which is not the case when the iodic acid is reduced by albuminous or other matters.
4. If a morphine salt be dissolved in strong sulphuric acid, and a drop of water added to heat the mixture, the subsequent addition of a drop of nitric acid will turn the liquid red, changing to green, and finally to brown.
5. When mixed with 6 to 8 parts of sugar and a drop of concentrated sulphuric acid added, salts of morphine exhibit a beautiful purple colour, changing gradually through blue, violet, green, and lastly yellow. Very dilute solutions are to be first saturated with sugar, the acid carefully poured in, and the colour observed where the liquids meet. Codeine resembles morphine in this reaction, but is distinguished by being readily taken up by chloroform from a solution mixed with excess of potassium hydrate, while morphine is not so dissolved.
6. Chlorine water and ammonium hydrate produce a red coloration, changing to brown, provided the solution does not contain less than $\frac{1}{1000}$ part of morphine.
7. It is precipitated by, but redissolved in excess of, all the alkaline hydrates. Its only certain precipitant being sodium hydrogen carbonate.
8. A solution made alkaline with ammonium hydrate gives a grass-green coloration on warming with ammonia-oxide of copper.

7. **Codeia** (*codeine*) resembles morphia, but is more soluble in water and ether.
   1. It is precipitated by the alkaline hydrates, very readily soluble in excess of ammonium hydrate, but insoluble in excess of potassium or sodium hydrates.
   2. HNO_3 produces a yellowish tinge.

8. **Narcotia** (*narcotine*) is insoluble in water, but slightly soluble in alcohol and ether. It is precipitated by potassium hydrate, insoluble in excess.
   1. Chlorine water and ammonium hydrate gives a yellowish-red liquid.
   2. H_2SO_4 gives, when heated, a red; intensified by adding a trace of nitric acid.
   3. Boiled with H_2SO_4 (dilute) and MnO_2, and filtered *hot*, the solution on cooling deposits crystals of opianic acid.

9. **Narceia** (*narceine*) is soluble in water and glycerin, less so in alcohol, and insoluble in ether and chloroform. It gives,—
   1. With dilute HCl a blue colour.
   2. With H_2SO_4 an amber changing to deep red.

10. **Meconia** (*Meconine*) is soluble in water, glycerin, and chloroform. Heated with H_2SO_4, it becomes first emerald-green and then purple.

11. **Thebaia** (*Thebaine*) is insoluble in alcohol, ether, and chloroform. With sulphuric acid it becomes blood-red.

12. **Papaverine** is slightly soluble in water, but freely in boiling alcohol. Cold sulphuric acid produces no colour, but on heating it is first purple and finally red.

13. **Strychnia** (*Strychnine*) is very slightly soluble in water and ordinary alcohol, but soluble in boiling rectified spirit. It is almost insoluble in ether, but freely soluble in chloroform and in amylic alcohol.

There are numerous tests for strychnine, but the following is the chief, and it is by it that strychnine is detected.

A little of the alkaloid is placed on a watch glass, and moistened with a drop of strong sulphuric acid, which dissolves it, without affecting it in any other way. Another drop of the sulphuric acid is then placed on another part of the watch glass, and a small crystal of potassium dichromate is placed in it. As soon as the dichromate communicates a colour to the acid, the two drops are caused to unite by drawing them together with a glass rod, when a magnificent, but evanescent, violet colour is immediately produced.

A similar effect is produced by using, instead of the dichromate, $K_6Fe_2Cy_{12}$, MnO_2, PbO_2, or the positive electrode of a galvanic battery.

14. **Brucia** (*Brucine*) is soluble in water, alcohol, and chloroform, but not in ether.

The presence of brucine is best recognised as follows:—

1. Strong sulphuric acid turns it red, yellow, and finally green, in rapid succession. Strychnine does not prevent the occurrence of this or the following reaction.
2. Nitric acid strikes a magnificent red colour, which is altered to violet and green by stannous chloride. This latter reaction serves to distinguish it from the morphine red.
3. Potassium iodide gives a kermes-coloured reaction in a solution of $\frac{1}{1000}$ part of brucine.

15. **Veratria** (*Veratrine*) is insoluble in water, but soluble in alcohol and ether. It is very irritant, and the smallest trace of it inhaled causes violent sneezing.

1. With cold H_2SO_4 it is not much affected; but warmed, it forms a resinous mass, dissolving to a deep-red fluid.
2. With strong HCl it gives no colour; but on warming becomes deep red.
3. Chlorine water tinges it brown, changing fainter on adding ammonium hydrate.

16. **Atropia** (*Atropine*) is slightly soluble in water, but freely in alcohol, ether, and chloroform. Its reactions are as follows:—

1. It powerfully dilates the pupil of the eye.
2. $AuCl_3$ produces a precipitate.
3. By heating with strong sulphuric acid till it turns brown. On the addition of a little water, a powerful odour of orange-flowers is evolved.
4. By boiling with potassium dichromate and dilute sulphuric acid, a liquid is produced, which, on the addition of excess of potash, gives a smell of herrings.
5. Phospho-molybdic acid yields a yellow precipitate, soluble in ammonium hydrate, and forming a blue solution.

6. A most characteristic test is the peculiar aromatic odour perceived on placing atropine on a few crystals of chromic anhydride—CrO_3—in a porcelain basin and applying a gentle heat till the mixture turns green.

17. **Beberia** (*Beberine*) is soluble in acids, forming a yellow solution which does not form crystalline salts. It is precipitated by potassium and sodium hydrates, and is freely soluble in ether.

Heated with H_2SO_4 and potassium dichromate, it forms a black resinous mass.

A curious characteristic is, that by friction with a piece of silk it becomes electrical, and will affect a galvanometer and attract very small pieces of light paper.

18. **Aconitia** (*Aconitine*) is only sparingly soluble in water. It is recognised as follows :—

1. By its causing a violet colour when added to phosphoric acid which has been evaporated over the water-bath to the thickness of a syrup.
2. When aconitine is stirred up with concentrated sulphuric acid and a drop of a saturated solution of sugar is added, a fine rose-tint is produced, changing to dirty violet and brown. There is a danger of this test being mistaken for the similar reactions with morphine and codeine, but morphine is not taken up by benzene from its solution in the presence of excess of potassium hydrate, while aconitine and codeine are so dissolved. Again, aconitine is sparingly soluble in water, codeine dissolving easily.
3. $AuCl_3$ gives a precipitate, but $PtCl_4$ does not.
4. Strong H_2SO_4 produces first a yellow, and then a fawn-brown.

19. **Delphinia** is similar to aconitia in most of its reactions, but in addition gives a violet-red with strong H_2SO_4 and bromine water.

20. **Colchicina** (*Colchicine*) is soluble in water and closely allied to veratria, but does not cause sneezing. *It is taken up by ether from an acid solution.* With HNO_3 it gives a deep violet.

SYSTEMATIC COURSE FOR THE DETECTION OF A SINGLE OFFICIAL ALKALOID.

All the reactions obtained must be afterwards confirmed by the other special tests.

1. Place a little of the alkaloid on a porcelain crucible lid, and add a drop of strong sulphuric acid.
   (*a*) Immediate bright red = **Salicin** (*although not an alkaloid, yet often present as an adulterant*).
   (*b*) On heating gently, first yellow, then orange, and finally cherry-red = **Veratria.**
   (*c*) Fawn brown colour, possibly **Aconitia** (confirm by syrupy H_3PO_4).
2. If the H_2SO_4 gave no colour, place on another part of the lid a minute crystal of potassium dichromate, add to it a drop of strong sulphuric acid, and draw the two drops together with a rod.
   (*a*) Evanescent blue-violet = **Strychnia.**
   (*b*) On diluting slightly and warming, a fragrant odour = **Atropia.**

3. To a fresh portion of the alkaloid on another lid add a drop of strong nitric acid.
   (*a*) Blood red, decolorized by warming and adding stannous chloride = **Morphia.**
   (*b*) Blood-red, turned violet by warming and adding stannous chloride = **Brucia.**
4. Dissolve in water by the aid of a drop of dilute hydrochloric acid, and add some chlorine water, and then ammonium hydrate in excess.
   (*a*) Green-coloured solution = **Quinia**
   (*b*) Yellowish-white precipitate = **Cinchonia.**

COURSE FOR THE DETECTION OF A MIXED SAMPLE OF ALKALOIDS.

1. Dissolve in water by the aid of a drop of hydrochloric acid, and shake up with ether.
   This may extract **colchicina** and a little **atropia.** Evaporate off the ether, and if it leave a residue, test it.
2. Add an excess of ammonium hydrate, shake up with chloroform, separate, and evaporate small portions of the chloroform solution to dryness at a time, and apply the simple table already given to the different residues thus obtained. All alkaloids may be present, except morphia.
3. Acidulate the liquid which has been shaken with chloroform, with acetic acid, and evaporate it to a low bulk at *a very gentle heat.* Add excess of a saturated solution of potassium hydrogen carbonate, and shake up with an ethereal solution of acetic ether. Evaporate off the ether almost spontaneously, and test the residue, if any, for morphia.

CHAPTER VII.

TOXICOLOGICAL ANALYSIS.

THIS subject is one which can only be treated in a comparatively short manner in the present work, as a full notice of all known poisons would be beyond its scope. As good general examples, however, we give the following processes for the more common poisons.

I. Poisonous Metallic Salts. Acidulate a portion of the contents of the stomach strongly with hydrochloric acid, place the whole in a basin over the water-bath, and drop in crystals of potassium chlorate until the contents of the basin are entirely decolorized. Boil up with the addition of some acidulated water if necessary, and filter, and use this solution for the ordinary separation course for metals, taking care to pass the sulphuretted hydrogen for several hours.

II. Mineral Acids are known by the highly-corroded appearance of the viscera and usually strongly acid reaction and free effervescence with sodium hydrogen carbonate. Warm the contents of the stomach with water, filter, and test for the acids.

III. Arsenic, Antimony, and **Mercury. Reinsch's Test.**—This process is performed as follows. The suspected liquid is acidulated with $\frac{1}{6}$ of its bulk of pure hydrochloric acid, boiled, and filtered. The filtrate is boiled with some fragments of bright copper foil, when a coating forms on the copper. The coated copper is then washed, dried carefully at a gentle heat, cut up into small fragments, and introduced into a small tube of hard glass. The mouth of the tube being lightly closed with the finger, the end containing the copper is strongly heated in the Bunsen or blowpipe flame. Arsenic sublimes as a white crystalline ring of arsenious anhydride, while antimony forms an amorphous sublimate of antimonious oxide, and mercury collects as a minute mass of metallic globules which can be caused to aggregate by rubbing with a glass rod. Should the sublimate possess the characters of arsenious anhydride the tube is filled with distilled water, boiled, and the solution thus obtained tested with argent-ammonium nitrate or cupr-ammonium sulphate. If the sublimate be amorphous and insoluble in water it is dissolved in tartaric acid, and the antimony precipitated from the solution by sulphuretted hydrogen.

IV. Arsenic and **Antimony** *only*. **Marsh's Test.**—A gas bottle is fitted up with a funnel tube and a jet, and some fragments of pure zinc are introduced. Dilute sulphuric acid is poured in by the funnel, and when the air has been expelled the hydrogen which issues from the jet is lighted, and a piece of cold porcelain is held in the flame. If no stain be produced on the porcelain, thus indicating that the reagents are perfectly pure, a little of the suspected fluid is added through the funnel tube, and after the lapse of a minute or two the cold porcelain is again held in the flame. If either arsenic or antimony be present, a stain will now be formed on the porcelain, for it always must be remembered that both antimony and arsenic produce the same re-

action. Several of these stains having been procured, they are treated one at a time by the following reagents:

REAGENTS.	ARSENIC STAIN.	ANTIMONY STAIN.
Solution of Calx Chlorata	disappears	not affected.
Ammonium Sulphydrate	very slowly affected	rapidly dissolves.
Bromine Vapour . . .	becomes yellow	becomes orange.
Heat (moderate) . . .	**disappears**	**remains.**

By another modification, the gas bottle is made to communicate first with a bottle containing plumbic acetate, and afterwards with one containing solution of argentic nitrate. The arseniuretted and antimoniuretted hydrogen having been freed by the lead from any possible contamination of sulphuretted hydrogen, pass into the argentic nitrate, in presence of which the former is decomposed, depositing silver and forming arsenious acid in solution, while the latter deposits as argentic antimonide. The precipitate, having been removed by filtration, is examined for antimony by boiling in solution of tartaric acid, and subsequent treatment with sulphuretted hydrogen; while the filtrate, on exact neutralization with dilute ammonium hydrate, deposits yellow argentic arsenite, should arsenic be present.

V. Arsenic only. Fleitmann's Test.—This process differs from Marsh's inasmuch as the nascent hydrogen required to convert the poison into arseniuretted hydrogen is evolved by heating zinc with a solution of potassium hydrate. A flask fitted up with delivery and funnel tubes is charged with the zinc and potassium hydrate, and heat being applied, the gas evolved is tested by exposing to its action as it issues from the delivery tube a piece of white filtering paper moistened with a solution of argentic nitrate. Should no stain be produced (indicating purity of reagents) a little of the suspected liquid is introduced by the funnel tube, and the process repeated, when, in the presence of arsenic, a dark stain will form on the paper. Further confirmation is obtained by heating the middle of the delivery tube to redness with a small spirit or gas flame, when the arseniuretted hydrogen will become decomposed, and deposit a mirror of arsenic on the cold part of the tube. This mirror may then be examined as already directed for such stains. Fleitmann's process is not applicable to antimony, as the hydrogen compound of that metal is not produced in presence of an excess of alkali.

VI. Oxalic Acid. Clarify the suspected matter by boiling with water, filter, and add plumbic oxy acetate to the filtrate, collect the precipitate on a filter, wash it, beat it up with water, pass sulphuretted hydrogen through the mixture until it smells freely of that gas, filter, wash the precipitate and expel the excess of the sulphuretted hydrogen from the filtrate by boiling, and concentrate on the water bath to a low bulk. The tests for an oxalate are then to be tried upon the clear liquid.

VII. Hydrocyanic Acid. This poison is often to be recognized simply by the smell, and is separated by taking advantage of its volatility. The usual way of proceeding is to put some of the suspected liquid into a flask, acidulated with sulphuric acid, and having inverted a watch glass, moistened with the test, over the mouth of the flask, to apply a gentle heat, when the vapour rises, and is absorbed by the reagent on the watch glass.

Another way is to distil the liquid with sulphuric acid, and having condensed the vapour in a receiver containing a little distilled water, to apply appropriate tests to the distillate.

These tests are three in number.

1. *The Silver Test.*—A drop of argentic nitrate exposed to the vapour of, or added to a solution, of prussic acid, gives a curdy white precipitate of argentic cyanide. The precipitate is soluble in ammonium hydrate and in strong boiling nitric acid, but not in dilute nitric acid; nor does it blacken on exposure to the light. Dried and heated it darkens, evolving half its cyanogen, leaving a mixture of silver and argentic paracyanide. During the action effervescence is observed, and a bright glow seems suddenly to pass through the mass.

2. *The Iron Test.*—A drop of solution of potassium hydrate is exposed to the action of the vapour, or an excess is mixed with the solution. To this a mixture of a ferrous and a ferric salt is added, and the whole acidulated with hydrochloric acid. If hydrocyanic acid be present *Prussian blue* will be formed.

3. *The Sulphur Test.*—A drop of *yellow* ammonium sulphydrate is exposed to the vapour, or added to a solution of hydrocyanic acid, and the whole evaporated to dryness at a very gentle heat, with the addition of a drop of ammonium hydrate. A residue is thus obtained which strikes a blood-red colour with ferric chloride, not dischargeable by hydrochloric acid, but at once bleached by solution of mercuric chloride. This colour is due to the formation of ammonium sulphocyanide (which takes place when an alkaline sulphur, containing excess of sulphur, is brought into contact with cyanogen).—

VIII. Strychnia. The common method of examination pursued in cases of poisoning by strychnine is that of Girdwood and Rogers. The suspected matter is freely acidulated with hydrochloric acid, evaporated to dryness, and the residue thoroughly exhausted by rectified spirit. This solution having been once more evaporated, the residue is treated with water, and the whole again filtered. The watery acid solution thus obtained is treated with a slight excess of ammonium hydrate, and shaken up with chloroform in a long narrow tube. After standing at rest, as much as possible of the chloroform solution of strychnine is drawn off, without disturbing the upper aqueous layer. The chloroform having been driven off by evaporation, the residue is digested for some hours on the water-bath with a few drops of *pure* strong sulphuric acid, which chars foreign organic matters but does not affect the strychnine. The mass, having been exhausted with water and filtered, is once more rendered alkaline by ammonium hydrate, and shaken up with chloroform, which on evaporation, will generally leave a residue of strychnine sufficiently pure for testing. Sometimes it is necessary to repeat the digestion with sulphuric acid and subsequent portions of the process before a residue of sufficient purity is obtained. The acid used must be perfectly free from nitrous compounds and should be tested and purified if necessary. The residue is sufficiently pure for testing when the addition of a drop of strong sulphuric acid causes no tinge of colour. (See tests for Strychnia, page 148.)

IX. Opium. The research in cases of poisoning by opium or a morphine salt is best conducted as follows. The suspected matter, having been cut up into small pieces, is, together with the fluid contents, warmed for some time with alcohol acidulated with acetic acid, and filtered. It is then precipitated with excess of plumbic oxy-acetate. The precipitate having been washed and marked A, and the filtrate having been marked B, are then examined separately as follows:—

1. A is mixed up with a little water, and sulphuretted hydrogen is passed through until the whole is decomposed. The resulting black mixture is filtered to remove plumbic sulphide, and the clear solution, having been concentrated until free from sulphuretted hydrogen, is tested with a drop of ferric chloride, when the development of a red colour, not destroyed by *dilute* hydrochloric acid or *by solution of mercuric chloride*, indicates the presence

meconic acid; thus leading to the inference that the poison employed was a preparation of opium.

2. B is treated with sulphuretted hydrogen in excess and the precipitated plumbic sulphide is removed by filtration. The solution, having been evaporated nearly to dryness on a water bath, is treated with a few drops of water and filtered. To the filtrate is added an excess of potassium hydrogen carbonate, and the whole is placed in a long tube and shaken up with an ethereal solution of acetic ether. The ether solution is then separated by a pipette and evaporated nearly to dryness at a very gentle heat, and finally allowed to dry spontaneously under a desiccator. The residue thus obtained is tested for Morphia. (See tests for Morphia, page 148.)

X. Poisonous Alkaloids generally. *Stas's process* consists essentially in :–

1. Heating the suspected viscera with twice their weight of absolute alcohol, to which about 30 grains of pure tartaric acid have been added ; filtering when cold, washing with absolute alcohol, and evaporating the solution *in vacuo*

2. The residue thus obtained is dissolved in the smallest possible quantity of water, and while still acid is shaken up in a tube with ether. The ethereal solution having been drawn off and preserved (see Table, *infra*) the remaining liquid is placed in a basin and powdered sodium hydrogen carbonate added until effervescence ceases.

3. The solution thus neutralized is again transferred to the tube and shaken up with five times its bulk of pure ether, and when all has settled clear, a little of the ether is evaporated, and the residue examined, to ascertain if the alkaloid be fixed or volatile, (1) by observing if it be in oily streaks, and (2) by warming very gently to about 100° F., and ascertaining whether or not any irritating fumes are driven off, in which case it is volatile.

CASE A.—*The alkaloid is apparently volatile and fluid.* Some strong solution of sodium hydrate is added to the contents of the flask, and the whole having been again shaken and allowed to settle, the ether is removed by a pipette, and the process of shaking repeated several times with fresh ether. The ethereal solutions having been united are shaken with a little dilute sulphuric acid (1 of acid to 4 of water) which causes the alkaloid to become a sulphate, in which state it is insoluble in ether, and consequently passes into the water. The ether having been poured away, the acid solution is treated once more with excess of sodium hydrate and ether as before, and the ethereal solution by careful spontaneous evaporation leaves the pure alkaloid.

CASE B.—*The alkaloid is fixed and solid.* The contents of the flask are treated, as in the last case, with sodium hydrate and ether, and the ethereal solution evaporated. A little alcohol is added to the residue to dissolve the alkaloid, and the solution thus obtained again evaporated. The residue is then converted into sulphate, and dissolved by adding a little water slightly acidulated with sulphuric acid. The solution thus obtained having been concentrated *in vacuo* over sulphuric acid to three-fourths of its bulk, is treated with pure potassium carbonate in slight excess and the mixture exhausted with absolute alcohol, which on evaporation leaves the alkaloid in a pure state.

The alkaloids thus obtained may be then separated by the following table devised by **Brunner.**

BRUNNER'S ALKALOID SEPARATION TABLE.

Absorbed by Ether from Acid Solution.*			Absorbed by Ether from Alkaline Solution. †									Remaining in Alkaline Solution.
With Tannin.			Solid (without odour).							Liquid (strong odour).		MORPHIA.
Precipitable.		Not precipitable	With concentrated sulphuric acid.				With concentrated sulphuric acid and bichromate of potassium.		With concentrated phosphoric acid on warming.	With chlorine-water.		
COLCHICINA.	DIGITALIN.	PICROTOXIN.	In the cold.		On warming.		In the cold.	On warming.	ACONITIA.	Precipitable.	Not precipitable.	
			Rose-red	Brownish red	First yellow, then orange and cherry red.	First yellow, then blue-violet and dark red.	Blue-violet.	Odour of flowers.		CONIA.	NICOTINA.	
			BRUCIA.	DELPHINIA.	VERATRIA.	NARCOTINA.	STRYCHNIA.	ATROPIA.				
Solution *yellow*; nitric acid colours it *violet*. If the nitric acid solution is diluted and made alkaline with NaHO, an *orange-red* coloration is produced.	Mixed with solution of ox gall and concentrated sulphuric acid a fine *red* zone is produced at first, afterwards a *red* liquid. — Dissolved in concentrated sulphuric acid and a trace of bromine added, a violet-red coloration appears.	The colourless solution in water containing soda is reduced by Fehling's copper-solution	Dissolves in concentrated nitric acid with a *light red* colour, which on warming changes to *yellow*, if then chloride of tin is added, a *blue violet* colour appears.	With concentrated sulphuric acid and bromine water *violet-red*. The same coloration appears on evaporating with phosphoric acid. *Aconitia* dissolves with *a brown-red* colour in sulphuric acid.	Dissolves in concentrated hydrochloric acid without colour, but on warming becomes fine *dark red*.	The solution in H_2SO_4 and on addition of a trace of HNO_3 is *red*, concentrated H_2SO_4, which contains a trace of molybdate of sodium is coloured, *green*. Dissolves in chlorine-water greenish white, but on adding NH_3 *yellow-red*.	Solution in HNO_3 *yellow*; the *blue-violet* colour appears also, when instead of the $K_2Cr_2O_7$, MnO_2, PbO_2, red prussiate of potassium or iodate of potassium is taken.	The fragrant odour appears more certain and distinct when a few crystals of chromic acid are placed upon the alkaloid and very gently warmed until green oxide of chromium begins to form	Produces a *violet* coloration. Is dissolved by concentrated sulphuric acid with a *fawn-brown* colour. — Delphinia and digitalin produce the same reaction with concentrated phosphoric acid.	Aqueous solution becomes coloured on warming — Dry muriatic acid gas colours it first *red*, then *deep blue*.	Aqueous solution not coloured on warming. — Becomes violet on gently warming with hydrochloric acid, if nitric acid is added, then the colour changes to *orange*.	The solution made alkaline with ammonia produces, on warming with ammonio-oxide of copper, a *grass-green* solution (Nadler). Concentrated nitric acid colours it *blood-red*, neutral perchloride of iron *dark blue*. When dissolved in concentrated sulphuric acid, warmed, allowed to cool, and some nitric acid added, an intense *red* colour appears. Reduces from a solution of iodic acid, iodine, which dissolves in bisulphide of carbon with a *violet* colour.

* Small quantity of Atropia.

† Also partially, Colchicina and Digitalin.

The complexity of **Stas's** process, and the facts that (1) conine is frequently lost by evaporation with the ether, and (2) that morphine, unless treated instantly and rapidly, refuses to dissolve in ether, has caused the proposition of many other processes. The best of which, as well as the most modern, is **Sonnenschein's process,** which depends on the fact that all ammonia derivatives are more or less easily precipitated by sodium phospho-molybdate in solution with nitric acid, which reagent is thus prepared. A solution of ammonium molybdate in water acidulated with nitric acid is precipitated by sodium phosphate. The resulting yellow precipitate, having been washed, is dissolved by heating with sodium carbonate. The solution is evaporated to dryness, ignited, moistened with a little nitric acid, and again ignited. The residue is dissolved in ten parts of water strongly acidulated with nitric acid, and kept for use in a stoppered and capped bottle to prevent any chance of the access of ammoniacal vapours.

The whole of the organic matter to be examined is repeatedly exhausted with very dilute hydrochloric acid: the extract is evaporated at a heat of 86° F. to the consistence of a thin syrup, then diluted, and left for some hours in a cool place before filtration. The filtrate is precipitated by excess of the above reagent, the precipitate collected on a filter, thoroughly washed with water containing the reagent, and introduced while moist into a flask. Barium hydrate is added, to a distinctly alkaline reaction; and the flask having been fitted with a delivery tube which is connected with a bulb apparatus containing hydrochloric acid, heat is gradually applied, when the volatile alkaloids distil over, and are collected in the hydrochloric acid. The residue in the flask (containing the fixed alkaloids) is freed from excess of barium hydrate by a current of carbonic anhydride, carefully evaporated to dryness, and extracted with strong alcohol. On evaporating the alcoholic solution, the alkaloids are commonly obtained in a state of such purity that they will at once exhibit their characteristic reactions; occasionally, however, they require to be further purified by recrystallization from alcohol or ether.

CHAPTER VIII.

VOLUMETRIC QUANTITATIVE ANALYSIS.

I. GENERAL PRINCIPLES.

In performing this variety of quantitative analysis the results are obtained by finding the quantity of any reagent capable of producing a given reaction. For example, supposing we take the equation,—

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

it is evident that one molecular weight of $AgNO_3$ (170) will exactly turn one molecular weight of NaCl (58·5) into insoluble argentic chloride. If, therefore, to a solution of sodium chloride we added slowly 170 grains of argentic nitrate dissolved in water, and the precipitation ceased just as the last drop fell in, it is plain that we must have had exactly 58·5 grains of sodium chloride in solution; or, supposing that a less quantity of argentic nitrate had been found necessary (say 10 grains), then the amount of sodium chloride present would be found by simple proportion, thus—

$$170 : 58{\cdot}5 :: 10$$

i.e., $\frac{10 \times 58{\cdot}5}{170} = 3{\cdot}441$ grains NaCl actually present in the solution.

The necessity of weighing out the reagent every time is avoided by the use of what are called *standard solutions*, that is, solutions of known strength. These are usually made on the metrical system by dissolving a certain number of grammes in one litre (1000 grammes) of water; when, however, the grain system is employed, ten times the quantity of both reagent and water are taken, because 1000 grains would be so small an amount of solution as to be not worth making. Standard solutions receive special names according to their strength, as follows:—

1. A **normal solution** contains one molecular weight in grammes dissolved in one litre of water, or ten molecular weights in grains dissolved in 10,000 grains of water.
2. A **semi-normal solution** contains half a molecular weight in grammes dissolved in one litre of water, or ten times the amount in grains dissolved in 10,000 grains of water.
3. **Deci-normal** or **centi-normal solutions** contain, respectively, $\frac{1}{10}$ or $\frac{1}{100}$ of the molecular weight in grammes in a litre, or ten times these amounts in grains in 10,000 grains of water.

II. APPARATUS USED.

These are very simple, and consist:—

1. Of a graduated tube, usually constructed to contain 100 cubic centimetres of water and marked at each c.c., or to contain 1000 grains of water and marked at each 10 grains, this latter space being usually called a *test*

measure. The instrument is called a **burette**, and is supported on a proper stand and provided at the bottom with a pinchcock, by pressing which the fluid can be allowed to pass out rapidly or in drops at will. The burette is provided with a small tube which just fits into it and is closed at both ends, and marked by a line running round the middle. Previously to sealing the top end, a little mercury is introduced, so as to weight the tube and cause it to float upright just under the surface of water. This appliance is called **Erdmann's Float**, and the line on it enables the reading of the amount of fluid expended from the burette to be made very accurately.

2. Of a long tube on a foot, closed with a glass stopper and made to contain 1 litre or 10,000 grains of water, according to the system of weight followed. It is graduated in spaces of 10 c.c. or 100 grains, and is used for **mixing the solutions, being called a test mixer.**
3. Of several flasks called **measuring flasks**, with marks on their necks, holding, when filled up to these marks, definite volumes of water, such as 100 c.c. or 1000 grains.
4. Of a set of **pipettes**, which are tubes with bulbs near the middle, drawn out to a jet at the lower end, and so constructed as to **deliver** fixed quantities of liquid, such as 10, 50, or 100 c.c., or 100, 500, or 1000 grains. The distinction between the use of the measuring flask and the pipette must be steadily kept in view—the former being only for *containing fixed volumes*, while the latter is for *delivering the same into any other vessel.*

III. PREPARATION OF THE STANDARD SOLUTIONS.

1. **Standard Solution of Oxalic Acid.** This is a semi normal solution made by dissolving 63 grammes of crystallized oxalic acid—$H_2C_2O_4.2H_2O$—in one litre of distilled water at 60°, or 630 grains in 10,000 grains of water. Although official, it is in many ways an objectionable solution, notably because it is so nearly saturated that in cold weather the oxalic acid will refuse to entirely dissolve, or, if dissolved by warming, it will separate out. It is therefore preferable to make the solution quadri-normal (*i.e.*, 31·5 grammes per litre), and then to divide the number of cubic centimetres used by two before calculating. In practice, most analysts prefer to use a standard solution (semi-normal) of sulphuric acid instead of the above.

One c.c. of Oxalic Acid solution contains ·063 gramme pure $H_2C_2O_4.2H_2O$.

2. **Standard Solution of Sodium Hydrate.** This is normal, and contains 40 grammes per litre of real NaHO (or 400 grains in 10,000 grains). As, however, sodium hydrate can never be obtained absolutely free from moisture and impurities, it is made indirectly as follows. The ordinary *liquor sodæ* of the shops is taken, and a burette is filled with it. 100 c.c. of standard solution of oxalic acid is placed in a beaker, a few drops of solution of litmus added, and the solution is run in from the burette until the red colour is just changed to a pale purple-blue. The number of cubic centimetres of sodium hydrate solution used is then read off from the burette, and *ten times this amount of the liquor sodæ having been placed in the test mixer, distilled water is added till the whole measures one litre.* If the process has been carefully conducted, 50 c.c. of this solution will exactly neutralize 50 c.c. of the oxalic acid solution, because by the equation—

$$H_2C_2O_4.2H_2O + 2NaHO = Na_2C_2O_4 + 4H_2O$$

we see that 126 of $H_2C_2O_4.2H_2O$ exactly neutralizes 80 of NaHO, and consequently—

as 126 : 80 : : 63 to 40

Therefore 1 c.c. of *normal* NaHO is exactly neutralized by 1 c.c. of *semi-normal* $H_2C_2O_4$.

One c.c. of Soda Solution contains ·04 pure NaHO.

3. **Standard Solution of Argentic Nitrate.** This is deci-normal, and is prepared by dissolving 17 grammes ($AgNO_3 = 170$) of argentic nitrate in one litre of distilled water, or 170 grains in 10,000 grains. It should be kept in the dark.

One c.c. of Silver Solution contains ·017 pure $AgNO_3$.

4. **Standard Solution of Iodine.** This is also deci-normal, and is prepared by dissolving 12·7 grammes ($I = 127$) of Iodine in about 400 c.c. of distilled water by the aid of 18 grammes of potassium iodide and then making up to 1 litre with distilled water (or 127 grains in 10,000 grains with 180 grains of KI). The potassium iodide has nothing to do with the real strength of the solution; and provided sufficient be used to thoroughly dissolve all the iodine, the quantity is quite immaterial.

One c.c. of Iodine Solution contains ·0127 pure I.

5. **Standard Solution of Sodium Thiosulphate** (*Hyposulphite*). This is also deci-normal, and is made so as to exactly balance the iodine solution. It contains 24·8 grammes (or 248 grains) of $Na_2S_2O_3.5H_2O$ in one litre (or 10,000 grains) of water. As, however, the commercial salt is never pure the solution has to be made, like the sodium hydrate, indirectly. About 28 grammes of commercial sodium hyposulphite are dissolved in a litre of water and a burette is filled with the resulting liquid. 100 c.c. of standard solution of iodine are then placed in a beaker, and the solution from the burette is added slowly until the colour begins to lighten. A few drops of mucilage of starch are then stirred in and the cautious addition of the hyposulphite continued until the blue colour is just discharged. The number of cubic centimetres used is then read off, and *ten times this amount having been placed in the test mixer, water is added till the whole measures one litre.* If the process has been carefully done, the equation—

$$2Na_2S_2O_3.5H_2O + I_2 = 2NaI + Na_2S_4O_6 + 5H_2O.$$

proves that 248 of real sodium thiosulphite decolorizes 127 of Iodine, and therefore, 12·7 of I represents 24·8 of $Na_2S_2O_3$. If, therefore, the solution is correct, it will decolorize the iodine solution exactly c.c. to c.c.

One c.c. of Hypo-sulphite Solution represents ·0127 pure I.

6. **Standard Solution of Potassium Dichromate.** This is viginti-normal, and is made by dissolving 14·75 grammes of $K_2Cr_2O_7$ in one litre of water (or 147·5 grains in 10,000 grains). It should be carefully checked as described further on. (See estimation of Fe.)

One c.c. of Dichromate Solution contains ·01475 pure $K_2Cr_2O_7$.

IV. CALCULATION OF RESULTS.

After the process is complete, the results may be calculated in two ways, either by full calculation or by the use of equivalents.

A. The full calculation is conducted as follows:—

1. Multiply the number of c.c. used by the strength of the standard solution in each c.c. = (*a*).
2. Draw the equation for the reaction, and by simple proportion calculate (*a*) from what it is, to what you want to know = (*b*).

3. Multiply (*b*) by 100, and divide by the quantity weighed out for analysis, and the answer (*x*) will give the percentage of the real article present in the sample.

For example, let us suppose that we took 4 grammes of commercial *soda caustica*, to ascertain how much real NaHO it contained. On finishing the proper process, we found that we used 90 cubic centimetres of oxalic acid solution.

1. $\cdot 90 \times \cdot 063 = 5 \cdot 67$ solid oxalic acid actually added.
2. $H_2C_2O_4 2H_2O + 2NaHO = Na_2C_2O_4 + 4H_2O$.

   Therefore as—

$$H_2C_2O_4 2H_2O : 2NaHO :: 5 \cdot 67$$
$$126 : 80 :: 5 \cdot 67$$

Or,

$$\frac{5 \cdot 67 \times 80}{126} = 3 \cdot 60 \text{ real NaHO in the amount taken for analysis.}$$

3. $\frac{3 \cdot 60 \times 100}{4}$ per cent. real NaHO in the sample of commercial *soda caustica* analysed.

9. The short method by equivalents. The term equivalent is used in volumetric analysis to represent the amount by weight of any body which corresponds to a given amount of the reagent, as shown by the equation. Thus, taking the same case as already illustrated, the equation—

$$H_2C_2O_4 2H_2O + 2NaHO = Na_2C_2O_4 + 4H_2O$$

shows that 126 (or 1 molecule) of oxalic acid requires 80 (or 2 molecules) of sodium hydrate for complete neutralization. But our standard solution of acid is semi normal, and consequently contains only half a molecule per litre; and therefore it would only neutralize one molecule of NaHO, because—

as 126 : 80 : 63 to 40.

63 grammes of oxalic acid used in any analysis will therefore represent 40 grammes of real NaHO. Taking now the following scale of strengths:—

1000 c.c.	(1 litre) of oxalic	acid contains	63	and represents	40	of NaHO
100 c.c.	do.	do.	6·3	do.	4·0	do.
10 c.c.	do.	do.	·63	do.	·40	do.
1 c.c.	do.	do.	·063	do.	·04	do.

The equivalent of NaHO in volumetric analysis by oxalic acid is, therefore, ·04 gramme for each c.c. of acid used.

The rule then follows: Note the number of c.c. used, and simply multiply that by the equivalent value for 1 c.c. of the substance analysed. Thus, in the example already studied, 4 grammes of *soda caustica* to 90 c.c. of oxalic acid; therefore—

$90 \times \cdot 04 = 3 \cdot 60$ amount of real NaHO in the 4 grammes of *soda caustica*, and

$$\frac{3 \cdot 60 \times 100}{4} = 90 \text{ per cent. real NaHO in the sample.}$$

For the full carrying out of this simple method, it is necessary to commit to memory the equivalent values as hereafter given for each analysis.

V. ESTIMATION OF ALKALINE HYDRATES.

A convenient quantity having been weighed out (taking care that the amount used cannot require more than 100 c.c. of the reagent) is diluted, if a liquid, or dissolved, if a solid, and a few drops of solution of litmus are added.

The beaker containing this liquid is then brought under the burette containing the standard oxalic acid, and the latter is run in until the blue colour changes to reddish purple. The number of c.c. used is then read off from the burette and calculated.

The proper amounts to take for analysis are thus given in the B.P. :—

Liquor ammoniæ	8·5	grammes
„ „ fort.	5·23	„
Liquor calcis	438·00	„
„ „ sacchar.	46·02	„
Liquor potassæ	46·29	„
„ sodæ	45·80	„
Potassa caustica	5·60	„
Soda caustica	4·00	„

The equivalent values of the alkalies for 1 c.c. of acid are as follows :—

1 c.c. of oxalic acid solution represents	·017 NH_3
1 c.c. do. „ do. „	·028 CaO
1 c.c. do. „ do. „	·056 KHO
1 c.c. do. „ do. „	·040 NaHO

VI. ESTIMATION OF ALKALINE CARBONATES.

Owing to the fact that the liberation of carbonic acid during the neutralization of a carbonate communicates a spurious acidity, and turns the litmus red before the proper point, it is necessary in this case to proceed as follows :— Weigh out and dissolve the carbonate, then add the litmus, and run in from a burette a considerable excess of oxalic acid, carefully noting the amount used. Boil the liquid in the beaker for some minutes, and see that it retains its red colour after boiling, because, if it does not, excess of acid has not been added. Now bring the whole under another burette charged with standard solution of sodium hydrate, and carefully add it until the liquid changes pale violet. Note the number of c.c. used, and deduct it from the total acid first added, when the difference will represent the true number of c.c. of standard acid used in neutralizing the carbonate, which is then to be calculated as usual.

The proper quantities of the B.P. carbonates to be taken for analysis are :—

Ammoniæ carbonas	5·9	grammes.
Potassæ carbonas	8·3	„
„ bicarbonas	5·0	„
Sodæ carbonas	14·3	„
„ bicarbonas	8·4	„

The equivalent values of the alkaline carbonates for each c.c. of acid are as follows :—

1 c.c. of standard oxalic acid represents	·059 $N_4H_{16}C_3O_8$
1 c.c. do. „ do. „	·143 $Na_2CO_3 10H_2O$
1 c.c. do. „ do. „	·084 $NaHCO_3$
1 c.c. do. „ do. „	·069 K_2CO_3
1 c.c. do. „ do. „	·100 $KHCO_3$

By using solution of cochineal as an indicator instead of litmus, the alkaline carbonates may be liberated directly just like the hydrates, as the presence of free CO_2 does not affect the colour of cochineal.

VII. ESTIMATION OF ORGANIC SALTS OF POTASSIUM AND SODIUM.

A weighed quantity of the substance is ignited in a small platinum crucible until fumes cease, by which it is reduced to the carbonate mixed with finely-divided carbon. The residue is dissolved in warm water, and a little litmus

having been added, it is treated with excess of standard oxalic acid, boiled, and checked back by standard sodium hydrate exactly as already described for the analysis of alkaline carbonates.

Convenient quantities to take, according to the B.P., are :—

Potassæ tartras	11·30 grammes
„ „ acida	18·80 „
Soda tartarata	14·10 „

The equivalent values of the salts for each c.c. of oxalic acid solution are as follows :—

1 c.c. of standard oxalic acid represents .	·113 $K_2C_4H_4O_6$
1 c.c. do. do. .	·094 $KHC_4H_4O_6$
1 c.c. do. do. .	·141 $KNaC_4H_4O_64H_2O$

VIII. ESTIMATION OF SALTS OF LEAD.

This is also conducted by means of standard oxalic acid, which is simply carefully run in until the precipitation of plumbic oxalate ceases.

Convenient quantities are :—

Plumbi acetas	3·80 grammes
Liquor plumbi subacetatis . . .	41·33 „

The equivalent values for each c.c. of standard oxalic acid are :—

1 c.c. of standard oxalic acid represents .	·1855 $Pb2C_2H_3O_23H_2O$
1 c.c. do. do. .	·137 $Pb_2O2C_2H_3O_2$

The oxalic acid solution is also used to take the alkalinity of borax and the strength of the effervescing liquors of potash and soda. The following are the empirical strengths they should exhibit :—

19·10	grammes of	borax	should take	100 c.c. oxalic acid
438·0	„	liq. potass. effervesc.	„	15 c.c. „
438·0	„	liq. sodæ effervesc.	„	17·8 c.c. „

IX. ESTIMATION OF FREE ACIDS.

This is performed by simply adding a few drops of solution of litmus, and running in standard solution of sodium hydrate until the red colour just changes to pale violet, then noting the number of c.c. used, and calculating.

The following are the quantities ordered to be taken for analysis by the B.P.

Acetum	44·54 grammes
Acid. Acetic.	18·20 „
„ „ dil.	44·00 „
„ „ glacial	6·00 „
„ Citric	7·00 „
„ Hydrochloric	11·48 „
„ „ dil.	34·50 „
„ Nitric	9·00 „
„ „ dil.	36·13 „
„ Nitro-hydrochlor. dil.	35·24 „
„ Sulphuric	5·06 „
„ „ aromat.	30·42 „
„ „ dil.	35·90 „
„ Tartaric	7·50 „

The equivalent values of the respective acids for 1 c.c. of the sodium hydrate solution are as follows:—

Acetic acid	·060 $HC_2H_3O_2$
Acetic acid (anhydrous)	·051 $C_4H_6O_3$
Citric acid	·070 $H_3C_6H_5O_7H_2O$
Hydrochloric acid	·0365 HCl
Nitric acid	·063 HNO_3
Nitric acid (anhydrous)	·054 N_2O_5
Sulphuric acid	·049 H_2SO_4
Sulphuric acid (anhydrous)	·040 SO_3
Tartaric acid	·075 $H_2C_4H_4O_6$

X. ESTIMATION OF HYDROCYANIC ACID.

A suitable quantity of the sample (27 grammes) is weighed out, and rendered distinctly alkaline with the *liquor sodæ*. It is then brought under the burette containing the standard solution of argentic nitrate, and the latter is cautiously run in with constant stirring, until a faint, permanent, white cloud is produced in the liquid.

When the silver solution is first added to the cyanide no precipitate is produced, owing to the formation of a soluble double cyanide of silver and sodium:

$$2NaCy + AgNO_3 = AgCyNaCy + NaNO_3.$$

On continuing to add the silver, a time arrives when, the double compound having been fully formed, it is in turn decomposed by excess of silver, and a white cloud of argentic cyanide is produced.

$$AgCyNaCy + AgNO_3 = 2AgCy + NaNO_3.$$

At the moment, therefore, when the precipitate appears, sufficient silver has been added to combine with *one half of the cyanogen present in the sample*, as is shown by the formula AgCyNaCy. It now only remains to read off the number of c.c. of silver used, and apply the calculation:—

$$\frac{(\text{c.c. used} \times \cdot 017) \times 54}{170} = \text{HCN present in the amount taken for analysis.}$$

Or, by the short method, the number of c.c. of silver solution used is multiplied by the equivalent value in HCN, which is ·0054.

ESTIMATION OF CHLORIDES, BROMIDES, AND IODIDES.

The chloride is weighed out, dissolved in water, and placed in a beaker over a sheet of white paper, and brought under the burette charged with the standard solution of argentic nitrate. Two drops of a solution of potassium chromate are then added, and the silver solution is very carefully run in, with constant stirring, until the solution in the beaker just changes from yellow to red. This indicates that all the chloride has been precipitated as argentic chloride. The red-coloured argentic chromate will not form until all the chlorides have been removed; but whenever this is attained, the least excess of silver solution turns the chromate red. Each c.c. of decinormal silver solution used will indicate ·00355 of chlorine.

Bromides and iodides may be treated in the same way, or the silver solution may simply be added with constant stirring till precipitation ceases. The B.P. only values potassium bromides by this process, and directs the use of 1 gramme, which should take 84 c.c. The equivalents for 1 c.c. of silver solution are ·008 Br. and ·0127 I.

XII. ESTIMATION OF COMMERCIAL ARSENIATE OF SODA.

Dry some of the commercial salt at a temperature of 300° Fah., when it should lose 40·38 per cent. of its weight. Take one gramme of the dried residue, dissolve it in water, and add 5·3 cubic centimetres of standard solution of sodium hydrate. Into this prepared liquid run, from a burette, the standard solution of argentic nitrate, until the brick-red precipitate of argentic arseniate ceases to form.

With regard to the volumetric test mentioned above, the reason for adding sodium hydrate solution previously to running in the argentic nitrate, is to ensure the precipitation of triargentic arseniate without any acid being set free, as would otherwise happen. It is necessary to secure the non-liberation of acid, because it would dissolve the argentic salt. With sodium hydrate the reaction is—

$$Na_2HAsO_4 + 3AgNO_3 + NaHO = Ag_3AsO_4 + 3NaNO_3 + H_2O;$$

which shows that $3AgNO_3$ (510) represents Na_2HAsO_4 (186) or $Na_2HAsO_4 7H_2O$ (312) or $Na_2HAsO_4 12H_2O$ (402).

The number of c.c. of silver used should therefore be multiplied by the equivalent value of Na_2HAsO_4 = ·0062.

XIII. ESTIMATION OF ARSENIOUS ACID.

This is performed by the standard iodine solution, which acts as an indirect oxidizer, the following reaction occurring:—

$$As_2O_3 + 5H_2O + 2I_2 = 2H_3AsO_4 + 4HI.$$

Thus it is plain that one molecular weight of arsenious acid represents four atomic weights of iodine; and therefore the calculation will require that the number of grain-measures of volumetric solution of iodine used be multiplied by ·0127 and 198 (the molecular weight of As_2O_3) and divided by 508 (four times the atomic weight, 127, of iodine).

The mode of estimation is very simple. Four decigrammes of arsenious anhydride are rubbed with about eight decigrammes of sodium hydrogen carbonate and a few drops of water in a beaker. The mixture is heated for a few minutes, and, an ounce or more of water having been added, the whole is boiled until complete solution is effected. The solution is allowed to become perfectly reduced to the ordinary atmospheric temperature, a little starch paste is added, and the iodine solution is run in until a slight permanent blue colour is produced. The number of c.c. of iodine used is read off, and the calculation made as follows:—

$$\frac{(\text{No. of c.c. used} \times \cdot 0127) \times 198}{508} = \left\{ \begin{array}{l} \text{amount of } As_2O_3 \text{ in the 4 decigrammes} \\ \text{taken.} \end{array} \right.$$

or more simply by multiplying the number of c.c. used by ·00495, which is the amount of As_2O_3 equivalent to 1 c.c. of the iodine solution. 44·15 grammes of liquor arsenicalis and liquor arsenici hydrochlorici thus treated should respectively take 80·8 and 81·0 c.c. of iodine solution.

XIV. ESTIMATION OF SULPHUROUS ACID.

When sulphurous acid is treated with iodine in the presence of water, it decomposes the latter, forming sulphuric acid and hydriodic acid:—

$$H_2SO_3 + I_2 + H_2O = 2HI + H_2SO_4.$$

The B.P. therefore uses standard solution of iodine for ascertaining, volu-

metrically, the strength of sulphurous acid, by adding it to a weighed quantity (3·47 grammes) of sulphurous acid, mixed with a little starch paste, until a permanent blue colour is produced (showing the presence of undecomposed iodine). The following calculation is then employed :—

$$\frac{(\text{No. of c.c. used} \times \cdot 0127) \times 82}{254} = \left\{ \text{amount of } H_2SO_3 \text{ in weight of sample taken.} \right.$$

$$\frac{(\text{c.c. used} \times \cdot 0127) \times 64}{254} = \text{amount of } SO_2 \text{ in weight taken.}$$

Or the number of c.c. used may be multiplied by ·0032, which is the equivalent value of SO_2 for 1 c.c. of iodine solution.

XV. ESTIMATION OF AVAILABLE CHLORINE

Is conducted in *calx chlorata* by the use of the standard solution of sodium hyposulphite. Weigh out 10 grammes of the sample of *calx chlorata*, and having rubbed it in a glass mortar with a little distilled water to a creamy consistence, wash the whole carefully into a large stoppered bottle or flask, and make up with water to one litre. Shake well for some time, and set it aside to settle. When clear, draw off with a graduated pipe the 100 c.c. for analysis, into a clean beaker. Thus you have $\frac{1}{10}$ of the whole soluble and active portion of 10 grammes (= 1 gramme) in the beaker. To this add 3 grammes of potassium iodide, and acidulate with 10 c.c. of hydrochloric acid, adding a few drops of starch paste.

The hydrochloric acid acts on the chlorinated lime to liberate the available chlorine.

$$CaCl_2Ca2ClO + 4HCl = 2CaCl_2 + Cl_2 + 2H_2O.$$

The chlorine then displaces an equivalent amount of iodine —

$$2KI + Cl_2 = 2KCl + I_2,$$

which instantly strikes a blue with the starch paste. The blue liquid is now to be brought under a burette charged with the standard *hyposulphite of soda* solution, which is to be carefully run in, until the colour is just discharged. This occurs by the formation of sodium iodide and sodium tetra-thionate :—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

As the hyposulphite solution represents ·0127 of iodine to each c.c., it follows that, 127 of I having been displaced by 35·5 of chlorine, nothing remains to be done but simply to multiply the number of c.c. of hyposulphite used by ·00355 the equivalent value in Cl for each c.c.

By the same process :—

6	grammes	of liquor calc.	chloratæ should take	50 c.c.	hyposulphite.
7	„	„	sodæ „ „ „	50 c.c.	„
43·9	„	„	chlori should take . .	75 c.c.	„

Good samples of calx chlorata should show 33 per cent. of available chlorine; but the B.P. considers it saleable so long as it shows 30 per cent.

XVI. ESTIMATION OF FERROUS SALTS

Is performed by means of the standard solution of potassium dichromate, which is a powerful direct oxidizer, and in presence of excess of acid raises iron from the ferrous to the ferric state. One molecule of this salt has the power in this manner to convert six atoms of ferrous iron. Thus with ferrous chloride and hydrochloric acid :—

$$6FeCl_2 + 14HCl + K_2Cr_2O_7 = 3Fe_2Cl_6 + Cr_2Cl_6 + 2KCl + 7H_2O.$$

Or, with sulphate and sulphuric acid :—

$$6FeSO_4 + 7H_2SO_4 + K_2Cr_2O_7 = 3Fe_23SO_4 + Cr_23SO_4 + K_2SO_4 + 7H_2O.$$

The standard solution being made, as already shown, by dissolving $\frac{1}{20}$ of a molecular weight (= 14·75 grammes) in one litre of water, each c.c. therefore contains ·01475 grammes of potassium dichromate, and is equal to ·0168 grammes of iron ($\frac{1}{20}$ of 6Fe).

The process is conducted as follows: Four ounces of water are introduced into a 10-ounce basin, placed over a lamp, and half an ounce of strong hydrochloric acid is added. When the whole is hot (not boiling), a weighed quantity of the iron compound is introduced, and as soon as it is dissolved the dichromate solution is run in, with constant stirring, until a drop taken from the basin on the end of the stirring rod fails to produce a blue colour when touched against a drop of potassium ferricyanide ; thus proving that the iron has been fully converted to the ferric state. Before commencing the experiment, a white porcelain slab should be covered with drops of the ferricyanide solution freshly made, and after each little addition of dichromate, a drop is to be taken out on the end of the rod, and tested on the slab.

This is most important, and so is the rapidity of working and application of the heat. In treating of this process it frequently happens that mention is not made of heat ; but the Author, who was educated under the late Professor Penny (the inventor of the process), learnt to work exactly as above directed. It is also important to remember that when the blue begins to lighten in colour, the dichromate must be added very carefully, as two or three drops are often sufficient to overdo and spoil the accuracy of the determination.

The number of c.c. used are read off, and having been multiplied by ·01475, the product is multiplied by as many molecules of the salt under analysis as will contain 6 atoms of iron, and divided by the molecular weight of potassium dichromate.

By the shorter method the number of c.c. used is multiplied by one of the following equivalent values,—

1 c.c. of standard $K_2Cr_2O_7$ (·01475) can convert				·0834	gramme	$FeSO_47H_2O$
,,	do.	do.	do.	·0348	,,	$FeCO_3$
,,	do.	do.	do.	·0358	,,	Fe_23PO_4
,,	do.	do.	do.	·0446	,,	Fe_23AsO_4
,,	do.	do.	do.	·0216	,,	$FeO(\text{in}Fe_3O_4)$
,,	do.	do.	do.	·0168	,,	Fe

XVII. ESTIMATION OF SUGAR.

To perform this operation, the following special solutions are requisite :—

I. A solution of the substance in which the glucose is to be estimated, containing *about* ·5 per cent. of that substance. This may conveniently be made by dissolving 5 grammes (of a syrup or any compound believed to contain 70 per cent. or more of glucose or lactose) in one litre of water.

II. *Fehling's* solution of cupric tartrate in potassium hydrate, made by dissolving 35 grammes of pure crystallized cupric sulphate, reduced to powder, and pressed between bibulous paper till absolutely free from extraneous moisture, in a little distilled water, and adding 173 grammes of sodium potassium tartrate (Rochelle salt), then introducing 60 grammes of pure potassium hydrate, dissolved in the smallest possible quantity of water, until the deep blue precipitate of cupric tartrate is entirely dissolved, using more of a ten per cent solution of potassium hydrate, if necessary. The liquid must then be made up to one litre, and immediately introduced into a well-stoppered bottle, as the carbonic anhydride of the air causes rapid deterioration. Previously to

every determination in which this solution is employed, it is necessary to boil a few drops with a quantity of pure water, and if any red precipitate is formed the solution must be rendered incapable of producing such (when boiled with pure water) by the addition of solid potassium hydrate free from carbonate. Thus made, Fehling's solution should represent ·05 gramme of glucose or ·0475 of sucrose for each 10 c.c.

III. A solution of 1 gramme of pure glucose, or ·95 gramme of pure lactose in 200 c.c of water. This solution, which is used for checking the Fehling's solution, must be made very exactly and carefully, as upon its accuracy the whole process depends. The *modus operandi* is as follows :

10 c.c. of Fehling's solution are put into four ounces of water contained in a porcelain basin, and the liquid is raised to the boiling point. The solution of sugar having been introduced into a burette, placed immediately over the basin, is then run in until the cupric solution, after five minutes' boiling, loses its colour. A drop of the solution is taken out with a glass rod, and let fall upon a piece of bibulous paper, placed over a beaker containing ammonium sulphide. If a black colour be produced, more sugar solution must be carefully added until this no longer occurs, which takes place when all the copper is thrown down as cuprous oxide. Between every two or three drops, the liquid must be boiled for three or four minutes before it is tested.

The number of c.c. of sugar solution employed having been read off, the following statement is made :—

As the number of c.c. used : 1,000 :: The number of c.c of Fehling's solution taken (= 10) : x.

Multiplying x by the amount of sugar to which a c.c. of the Fehling's solution corresponds, the product gives the total quantity of pure glucose in the litre of solution. If it be 5 grammes (the amount dissolved in the litre of water originally) the glucose taken for analysis is pure. If it be less, the quotient obtained by division by ·5 (viz., multiplication by 2), gives the percentage. If it be more (than 5 per 1000), which may occur when the check is made, the Fehling's solution must be too weak. In this case then the ratio of the amount employed to 5 is that which must be taken to reduce the volume of Fehling's solution to the true volume, that is, to the volume which would have been taken had it been of accurate strength.

Both the check and the actual estimation are carried out as above detailed.

When cane sugar is to be estimated, it must be first "inverted" by boiling for some hours with a few drops of dilute sulphuric acid, and then neutralized with sodium hydrate before using "*Fehling.*"

XVIII. ESTIMATION OF UREA.

The best way of estimating the amount of urea in urine is by means of mercuric nitrate, with which it causes a precipitate. The process is of some importance to pharmacists, and is thus performed :—

1. A solution of mercuric nitrate is prepared by dissolving 77·2 grammes of perfectly pure mercuric oxide in the smallest possible quantity of nitric acid; evaporating to get rid of all free acid, and diluting to one litre (if a precipitate of yellow *basic nitrate* should form, it may be redissolved by the addition of a drop of free nitric acid). This solution is so constructed that 1 c.c. will precipitate ·01 gramme of urea.

2. A mixture of two volumes of cold saturated solution of barium hydrate with one volume of a similar solution of barium nitrate.

3. Solution of sodium carbonate.

50 c.c. of the urine to be tested are mixed with 25 c.c. of the solution No. 2 which removes, by precipitation, all the phosphates and sulphates, and the whole is filtered. 15 c.c. of the filtrate (= 10 c.c. of the original urine) are

then put into a beaker, and brought under the burette containing the mercuric solution. The latter is now carefully run in, until all the urea is precipitated, which is known when a drop taken out of the beaker on a glass rod strikes a yellow colour with a drop of the sodium carbonate solution, placed upon a glass slab, over a piece of black paper to show the colour better. The number of c.c. of mercurial solution used are then read off, multiplied by ·01, which gives the urea in 10 c.c., and that × 10 = percentage.

In urine analysis it is more common, however, to state results in parts in 1000, instead of in percentages.

The mercuric solution should always be tested by a solution of 10 grammes of pure artificial urea in 1 litre of water, of which each c.c. will equal ·01 urea, and which should exactly balance the former, c.c. to c.c. There are certain difficulties which might sometimes occur, for which we must refer the student to *Sutton's Volumetric Analysis;* but we may mention that should the urine contain albumen, it must be first removed by boiling 100 c.c. with 4 drops of acetic acid, letting the coagulated albumen settle, and taking 50 c.c. of the clear urine for analysis.

XIX. ESTIMATION OF PHOSPHORIC ACID

Is performed by means of a standard solution of uranic nitrate in the presence of sodium acetate. The necessary solutions are,—

1. Standard solution of uranic nitrate, made by dissolving 70 grammes in 900 c.c. of water, and then, after ascertaining its strength by performing an analysis on 50 c.c. of the standard phosphate solution, diluting with water so that 50. c.c. will correspond exactly to 50 c.c. of that solution. If absolutely pure uranic nitrate were obtainable, theory requires the solution of 71 grammes in one litre of water to yield a solution which will balance the standard phosphate (each 1 c.c. = 1 gramme of P_2O_5).

2. **Standard phosphate solution,** made by dissolving 50·42 grammes of perfectly pure disodium hydrogen phosphate in one litre of water, when each c.c. will equal ·1 gramme of P_2O_5

3. A solution of 100 grammes of sodium acetate and 100 grammes of acetic acid in water, and the whole diluted to one litre.

4. Finely powdered potassium ferrocyanide.

To perform the process, the solution of the phosphate in about 50 c.c. of water, is placed in a basin on the water bath, mixed with 5 c.c. of solution No. 3 (sodic acetate), and No. 1 (uranic nitrate) is run in from a burette, until a drop taken from the basin on to a white plate just givesa brown colour when a little powderd ferrocyanide is cautiously dropped into its centre. The number of c.c. of uranic solution used having been noted, the usual calculations are to be applied.

After repeated trials upon 50 c.c. of the standard phosphate solution, so as to thoroughly adjust the strength of the uranic solution, and at the same time accustom the eye to observe the exact moment of the appearance of the brown coloration, the process may be practically applied to **Manures.**

The best method of preparing the solution of the manure, is to heat 10 grammes to dull redness for 15 minutes, and when cold to reduce it to a fine powder in a mortar, and add gradually 10 grammes of sulphuric acid diluted to 200 c.c. with water. Rinse the whole into a stoppered bottle, and make up with water to one litre. Shake up occasionally for an hour, and having then let all settle for three hours, draw off 100 c.c (= 1 gramme manure) for analysis. To this add a little citric acid (10 drops of a cold saturated solution), and slightly supersaturate with ammonium hydrate. Again acidify with acetic acid, add 10 c.c. sodium acetate solution, and then use the uranic solu-

tion as usual. If all these quantities be rigorously adhered to, each c.c. of uranic solution used can, without further calculation, be taken as indicating one per cent. of tricalcium phosphate in the manure.

This process is highly recommended by Mr. Sutton, of Norwich, and elaborate details will be found in his work on Volumetric Analysis.

XX. VALUATION OF MANGANESE PEROXIDE.

When manganic peroxide is treated with oxalic acid and sulphuric acid, it dissolves, forming manganous sulphate, converting the oxalic acid entirely into carbonic anhydride and water :—

$$H_2C_2O_4 + MnO_2 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O.$$

This reaction is taken advantage of to estimate the value of samples of the ore. The solutions required are,—

1. The B.P. volumetric solution of oxalic acid, made by dissolving 63 grammes of oxalic acid in one litre of water, each c.c. of which contains ·063 gramme oxalic acid.

2. A solution of potassium permanganate, of about the colour of strong port and water. 10 c.c. of the oxalic acid are introduced into a beaker, diluted to 200 c.c. with water, and acidulated with 5 c.c. of strong sulphuric acid. The permanganate is then run in carefully from a burette, until its colour ceases to be destroyed, and the contents of the beaker exhibit a faint permanent pink colour when viewed over white paper. The number of c.c. of permanganate used is carefully noted, and its relation to the oxalic acid thus ascertained.

We will suppose, for example, that 40 c.c. were required, then 40 c.c. of permanganate will represent 10 c.c. of oxalic acid. Having obtained the strength of our permanganate (which spoils by keeping, and therefore must be titrated and standardized every time), we proceed as follows :—

Weigh out 2 grammes of the sample to be analyzed, transfer it to a beaker, run in 50 c.c. of oxalic acid, and acidulate with 5 c.c. of strong sulphuric acid. The reaction immediately sets in, and carbonic anhydride is evolved with effervescence. The manganic peroxide dissolves, and in so doing decomposes an equivalent quantity of oxalic acid. The action is assisted at the last by gently heating, till no more gas is evolved, and the ore is all dissolved. The solution is diluted to 200 c.c., and 5 c.c. of sulphuric acid having been added, permanganate is run in until it ceases to be decolorized. The number of c.c. of permanganate used are calculated for the amount of oxalic acid they have been found to represent, and thus the quantity which has been decomposed by the ore is ascertained.

Example.—2 grammes of ore, treated with 50 c.c. of oxalic acid, took, after solution, 20 c.c. of permanganate. Now, as 40 c.c. of the latter were found to be equal to 10 c.c. oxalic acid, 20 must be equal to 5. Then $50 - 5 = 45$ c.c. of oxalic acid decomposed by the ore. 45 c.c. $\times$ ·063 = 2·835 oxalic acid, decomposed by 2 grammes of ore. Then from the equation already given,

$$\frac{2{\cdot}835 \times 87}{126} = 1{\cdot}957 \text{ pure peroxide in two grammes of ore;}$$

$$\text{and } \frac{1{\cdot}957 \times 100}{2} = 97{\cdot}85 \text{ per cent. peroxide in ore analyzed.}$$

For all the other many processes of volumetric analysis, the student is referred to any standard work upon the subject.

CHAPTER IX.

GRAVIMETRIC QUANTITATIVE ANALYSIS.

I. PRELIMINARY REMARKS.

BEFORE giving the processes for the quantitative estimation of the various metals, we must first say something about the preparation of filters, and the washing, drying, and weighing of precipitates.

1. THE PREPARATION OF FILTERS.

Ready-cut filters may be procured from the dealers in chemical apparatus. The kind known as Swedish is the best for all cases where the precipitate is finely divided or pulverulent. For gelatinous precipitates, such as ferric hydrate and calcium phosphate, the white English filters are preferable, but they should never be used, say, for barium sulphate or calcium oxalate, as those bodies would very likely pass through the pores of the filter, and so cause a loss in the analysis. The only drawback to Swedish papers is their filtering rather slowly. Whatever paper be used, the size for quantitative operations is, for the larger sort, six inches in diameter, for the smaller, about two inches. The small sort is used where we have to deal with traces of precipitate only, or when a small quantity of fluid has to be filtered. The paper should yield nothing to dilute acids, and if the ash exceed one milligramme per large filter it will in most cases be remedied by placing, say, 100 cut filters for some hours in a basin filled with a mixture of one volume of HCl and eight volumes of water. They must then be repeatedly washed with distilled water till quite free from acidity, otherwise they would crumble to pieces when being folded. The washing is a very tedious operation indeed, and having been completed, the basin is put on to a water-bath till the filters are perfectly dry, when they are taken out and their ash estimated.

This is most conveniently done by folding ten filters into a small compass, twisting a long platinum wire round the packet so as to form a cage, holding the free end in the hand and the paper over a previously weighed platinum crucible while touching it with the flame of a Bunsen burner. The paper burns and the ash drops into the crucible, while any particles of carbon which have escaped combustion are quite consumed by exposing the crucible for some time to a red heat till the ash gets perfectly white. The crucible after cooling is reweighed, and its increase is the ash of ten filters. Divided by ten, we get the ash of one filter; and in every case where both filter and precipitate are burned, the ash of the filter thus found must always be deducted from their total weight, and the difference is then the actual weight of the precipitate.

2. THE WASHING OF PRECIPITATES.

When the precipitate has been fully formed and the supernatant fluid has become quite clear, the latter is poured on the filter, care being taken not to

disturb the precipitate. After thus pouring off as much as practicable, the precipitate remaining in the beaker is treated with water and well stirred. When the whole has once more settled, the clear fluid is again passed through the filter. This operation having been repeated three or four times, the precipitate is allowed to pass on to the filter, any particles which stick to the sides of the beaker being removed with a feather; and the whole having been thus collected, the washing is continued by means of a washing-bottle, till the precipitate is quite freed from its soluble impurities. For instance, in estimating sulphuric acid, the barium sulphate is washed till the filtrate no longer gives a turbidity with argentic nitrate.

Many bodies, as ferric and aluminic hydrate, most phosphates, barium sulphate, and some of the carbonates are best washed with boiling water. Others, on the contrary, must be washed with cold water, such as plumbic sulphate, for which we use cold water acidified with some H_2SO_4; magnesium ammonium phosphate, for which cold dilute ammonium hydrate is used, etc.

3. DRYING OF PRECIPITATES.

After the precipitate has been thoroughly washed, the funnel containing it is loosely covered over with filter paper and then put into an air-bath. Most precipitates require a temperature of 212° F., but some of them, as magnesium ammonium arseniate, require a temperature of 220° F. before becoming constant in weight; while palladious iodide must be dried at a temperature not exceeding 200° F. Prolonged and repeated drying is only necessary when the precipitate is weighed on the filter.

4. IGNITING AND WEIGHING OF PRECIPITATES.

Most precipitates must first be ignited before they can be weighed. This is to drive off water which they may still retain after drying at 212° F., or carbonic anhydride and water. For instance, zinc is best weighed as oxide, and therefore the precipitate, consisting of oxycarbonate, is first ignited. Iron is precipitated as hydrate, but the composition of that body not being constant it is ignited and so made into pure oxide before weighing. As soon, therefore, as the precipitate appears dry it is carefully detached from the filter and put into a previously ignited and weighed crucible, the filter is burned on the lid (which has been weighed together with the crucible), the ash is thrown into the crucible, and the latter covered with the lid. The crucible is now supported by a pipe-clay triangle, and gently ignited at first to prevent spurting from the sudden evolution of steam or other gases. The lid is now taken off, and the crucible inclined a little so as to give a free access of air. The ignition is continued for some minutes, and the crucible, having been again covered with the lid, is allowed to cool and weighed. For accurate estimations it is best to let it cool under a desiccator.

The heat of an ordinary Bunsen burner is generally sufficient for all purposes; but the conversion of calcium carbonate into oxide requires the aid of a gas blowpipe; while argentic chloride must be heated with a rose Bunsen or spirit lamp until it just begins to fuse. The filters are, as already shown, burned separately, to prevent any reduction of the precipitate by the carbon of the filter.

Some precipitates are not ignited but weighed on a previously tared filter. Before weighing the filter (for which purpose it is placed between two closely-fitting watch-glasses provided with a clamp to hold them together) it must first be dried for fifteen minutes at 212° F. After drying the precipitate, the filter is again placed between the glasses and reweighed; the increase shows, of course, the weight of the substance. It is well to replace the filter

in the bath for, say, half an hour, and to weigh again. Should the weight be considerably less, it must be once more put into the bath and reweighed. As examples of precipitates weighed in this manner, we mention the sulphides of mercury and arsenic, which cannot be ignited because they would volatilize; magnesium ammonium arseniate, which would suffer a loss of arsenic in ignition; and potassium platino-chloride, which would partly decompose.

II. GRAVIMETRIC ESTIMATION OF METALS.

ESTIMATION OF SILVER.

(*a*) As Argentic Chloride.

Silver is most conveniently weighed as chloride, because this body is perfectly insoluble in water and dilute acids, and separates readily. The silver solution to be estimated is strongly acidified with nitric acid, which, for physical reasons, promotes the separation of the chloride, and a slight excess of hydrochloric acid is added. It is best to have the solution slightly warm, and to stir till the supernatant liquid has got perfectly clear. A little more hydrochloric acid is added, to make sure that all the silver is precipitated. The clear fluid is now poured off, but best through a filter, lest some particles of chloride should be accidentally carried away. The chloride, which must be kept from the light, is then washed by decantation with boiling water till every trace of acid is removed, the water poured off as completely as possible, and the chloride transferred into a weighed porcelain dish, dried, heated till it just commences to fuse, and weighed. The filter is burned on a lid, and should any excess of ash be obtained, this must be considered as metallic silver, because the *traces* of chloride are reduced by the filter paper. Or the ash may be treated with a drop of aqua regia, the resulting chloride dried, and its weight added to the other weight. The following calculation is now applied :—

$$\frac{\text{Weight of chloride} \times 108}{143.5} = \text{silver in the amount taken for analysis.}$$

(*b*) As Metal.

If silver is required to be estimated in organic salts, and other bases are absent, the analysis is performed by igniting a weighed quantity of the salt, and weighing the ash, which will consist of pure metallic silver.

ESTIMATION OF LEAD.

(*a*) As Plumbic Oxide.

Lead is usually estimated in this form. The solution containing the substance to be analyzed is precipitated with ammonium carbonate in the presence of a little ammonium hydrate. The precipitated plumbic carbonate is then collected on a small filter, washed, and dried. The dry precipitate is removed as completely as possible from the filter-paper, and introduced into a weighed porcelain crucible. The filter having been burned on the lid, and its ash added to the contents of the crucible, the whole is ignited, cooled, and weighed. By ignition, the oxide is formed; and after deducting the weight of the crucible, the following calculation is applied :

$$\frac{\text{Weight of precipitate} \times 207}{223} = \begin{cases} \text{weight of metallic lead in} \\ \text{amount of sample analyzed.} \end{cases}$$

Great care must be taken in the removal of the precipitate from the filter, as the carbon of the paper is apt to reduce the oxide to metallic lead, and thus cause loss of weight. The oxide must be completely soluble in warm acetic acid. Any insoluble substance may be metallic lead.

(*b*) As Plumbic Sulphate.

Lead is estimated as sulphate when it has to be separated from other metals which are not precipitated by sulphuric acid. The solution,—for instance, a weighed quantity of an alloy,—dissolved in nitric acid is mixed in a glass basin with a slight excess of sulphuric acid. As plumbic sulphate is slightly soluble in nitric acid, the whole is evaporated in the water-bath till acid fumes cease to be evolved. The sulphate is now washed by decantation with very dilute sulphuric acid, to remove other metals, then brought on the filter, and finally washed with spirit of wine. The sulphate is slightly soluble in water, but insoluble in dilute sulphuric acid, and altogether so in alcohol. The filter is now dried, the sulphate having been detached from it, the latter is put into a weighed porcelain crucible, ignited, and weighed. The filter is burned separately (best in another weighed crucible) the ash is treated with a drop of nitric acid and a drop of sulphuric acid, dried, ignited, and reweighed. The treatment with acid is necessary, because the sulphate is almost completely reduced to metallic lead or sulphide of lead by the carbon of the burning filter. The total weight of sulphate having been got, the following calculation is applied :—

$$\frac{\text{Weight of precipitate} \times 207}{303} = \text{lead in the quantity taken for analysis.}$$

ESTIMATION OF MERCURY.

(*a*) As Mercurous Chloride.

Compounds of mercury insoluble in water are dissolved in cold dilute HCl, and if this fails, they are treated with potassium hydrate solution, and chlorine gas is passed through the liquid till perfectly saturated. The excess of chlorine is expelled by gentle boiling. If mercury compounds were boiled with hydrochloric acid and potassium chlorate, a little of the mercury would volatilize.

To the solution some hydrochloric and phosphorous acids are added; and after standing for 12 hours in a warm place, the precipitated mercurous chloride is collected on a weighed filter, washed, dried at 212° F., and weighed.

$$\frac{\text{Weight of precipitate} \times 200}{235 \cdot 5} = \left\{ \begin{array}{l} \text{amount of mercury in the} \\ \text{sample taken for analysis.} \end{array} \right.$$

(*b*) As Mercuric Sulphide.

Through the solution of the mercuric salt a current of H_2S is passed till the liquid is saturated. It is necessary the mercury should be all in the mercuric state, and not contain other metals precipitable by H_2S. The precipitate is collected on a weighed filter, washed first with water, then with absolute alcohol, and finally, to remove any free sulphur, with a mixture of equal parts of ether and carbon disulphide. After drying at 212° F. and weighing, the following calculation is applied :—

$$\frac{\text{Weight of the sulphide} \times 200}{232} = \left\{ \begin{array}{l} \text{mercury in the sample} \\ \text{taken for analysis.} \end{array} \right.$$

ESTIMATION OF CADMIUM.

(*a*) As Cadmium Oxide.

The solution containing the metal is mixed with excess of sodium carbonate and boiled. The precipitated cadmium carbonate is collected upon a filter, washed with hot water, and dried. It is of the utmost importance to have a very thin filter, and to detach the precipitate as completely as possible from it. The filter is moistened with a little strong solution of ammonium nitrate, and dried, and a platinum wire having been twisted round it, it is then burned, the ash being allowed to drop into the crucible. The nitrate will cause a more speedy and complete oxidation of the carbon of the filter, and so prevent reduction of the oxide and volatilization of metallic cadmium. Yet, notwithstanding this precaution, a little loss is unavoidable. The crucible is now heated to redness, and after cooling the residual oxide is weighed.

$$\frac{\text{The weight of oxide} \times 112}{128} = \left\{ \begin{array}{l} \text{cadmium in the quantity} \\ \text{taken for analysis.} \end{array} \right.$$

(*b*) As Sulphide.

The solution is precipitated with ammonium hydrate and ammonium sulphide. The cadmium sulphide is collected in a weighed filter, washed, dried at 212° F., and weighed. This process is only applicable in the absence of metals also precipitable by ammonium sulphide. In the presence of metals of the fourth group, the solution must be slightly acidified with hydrochloric acid and precipitated by a current of sulphuretted hydrogen.

$$\frac{\text{Weight of sulphide} \times 112}{144} = \text{cadmium in the amount taken for analysis.}$$

ESTIMATION OF COPPER.

(*a*) As Cupric Oxide.

Copper is frequently estimated in this form. The solution (freed from other metals if necessary) is boiled with a slight excess of sodium hydrate. The precipitate is filtered out, washed, and dried. It is then carefully removed from the paper to a weighed crucible, and the filter having been burned on the lid, and the ash added to the contents of the crucible, the whole is well ignited, cooled in a desiccator, and weighed rapidly, because cupric oxide is very hygroscopic. To make sure that the oxide contains no suboxide, it is, however, generally moistened with a little fuming nitric acid, dried with the lid on and ignited for ten minutes, and then re-weighed; but this operation requires great care, and is liable to involve a loss on account of spurting.

$$\frac{\text{Weight of oxide} \times 63{\cdot}5}{79{\cdot}5} = \text{Copper in the quantity of substance analyzed.}$$

(*b*) As Metallic Copper.

The solution, which must be free from metals precipitable by zinc, is introduced into a weighed and very clean platinum basin. A small piece of zinc is introduced, and the crucible covered with a lid to prevent spurting. The solution must contain a slight excess of hydrochloric or sulphuric acid, but on no account nitric acid. After the fluid has become quite colourless and the basin has become coated with metallic copper, a little more hydrochloric acid is added, to dissolve out the excess of zinc, which will have disappeared when the liquid has ceased to effervesce. The fluid is now poured off, and the

copper repeatedly washed with boiling water till all acidity is removed. The basin is finally rinsed with absolute alcohol, quickly dried, and weighed. This process gives excellent results when pure zinc is at disposal; but it must be borne in mind that so-called pure zinc in rods frequently contains traces of lead insoluble in hydrochloric acid.

ESTIMATION OF BISMUTH.

(*a*) As Bismuth Oxide.

Bismuth is estimated in this form. The solution for analysis (freed, if necessary, from other metals) is diluted with water, and precipitated with a slight excess of ammonium carbonate. The precipitated bismuthous oxycarbonate is collected, washed, and dried. It is then separated from the filter paper, and the latter having been burned on the lid of a weighed crucible, the whole is introduced into the crucible, and ignited, cooled, and weighed. The weight of the crucible having been deducted, we say,—

$$\frac{\text{Weight of precipitate} \times 416}{464} = \left\{\begin{array}{l}\text{weight of bismuth in the quantity}\\ \text{of substance taken for analysis.}\end{array}\right.$$

(*b*) As Bismuth Sulphide.

Bismuth is sometimes estimated as sulphide; but this process cannot be much recommended, as the sulphide is apt to increase in weight on drying, owing to the absorption of oxygen. When following this method, a current of sulphuretted hydrogen is passed through the acid bismuth solution; the resulting sulphide is collected on a weighed filter, dried at 212° F., and weighed.

$$\frac{\text{Weight of the sulphide} \times 416}{512} = \left\{\begin{array}{l}\text{amount of bismuth in the}\\ \text{sample taken for analysis.}\end{array}\right.$$

ESTIMATION OF GOLD.

(*a*) As Metallic Gold, by Precipitation.

The solution is boiled with excess of ferrous sulphate or oxalic acid, and, to prevent iron compounds or oxalates from precipitating, some hydrochloric acid is also added. If oxalic acid is used, a slight effervescence will be noticed, so it is advisable to cover the beaker with a glass. The precipitated gold is washed on a filter, dried, ignited, and weighed. This method gives accurate results, providing the gold exists as trichloride.

(*b*) By Cupellation.

Gold solutions containing potassium cyanide are treated as follows: A known portion is evaporated with a few grammes of red lead. When dry, the crucible is covered and heated to redness. The result is a button of lead containing the gold, from which the latter is readily separated by cupellation, and can then be weighed.

ESTIMATION OF PLATINUM.

As Metallic Platinum.

Platinum is usually estimated in this form. The solution, which must contain the platinum as trichloride, is concentrated and precipitated with excess of ammonium chloride. As ammonium platino-chloride is slightly soluble in water, four times its bulk of absolute alcohol is added to the fluid, which, after standing for several hours, is filtered. The precipitate is well washed with spirit of wine, dried, ignited, and weighed, as metallic platinum.

Sometimes it is useful to wash the platinum on a filter with hot water, and to again dry and weigh. The results are accurate.

ESTIMATION OF TIN.

(*a*) As Stannic Oxide.

Alloys containing tin, but free from antimony or arsenic, are treated with nitric acid, which converts the tin into oxide, and other metals into nitrates. The acid fluid is evaporated nearly to dryness, the residue taken up with water and a little nitric acid; the oxide is washed by decantation, collected on a filter, completely washed and dried. It is then as completely as possible detached from the filter, the latter is burned on a lid, the ash added to the contents of the crucible, and the whole ignited. After cooling the oxide is moistened with a little nitric acid, dried (with the lid on), and again ignited, when, after cooling, it is ready for weighing.

Where we have to deal with tin in solution, the following method is applied:

The solution, which must be free from metals of the first three groups, is precipitated with sulphuretted hydrogen, the resulting sulphide is washed with solution of acetate of ammonium, which will prevent the stannic sulphide from passing through the filter. After drying, the sulphide is transferred to a weighed crucible, the filter burned on the lid, its ash added to the contents of the crucible, and the whole ignited, *at first very gently*, until fumes of sulphurous anhydride cease, and then at a very high temperature, with the addition of a fragment of ammonium carbonate. The whole having been cooled, weighed, and the weight of the crucible deducted, we say,—

$$\frac{\text{Weight of precipitate} \times 118}{150} = \left\{\begin{array}{l}\text{amount of metallic tin in the quantity}\\ \text{of substance taken for analysis.}\end{array}\right.$$

This process depends on the conversion of the sulphide into SnO_2 by ignition; but it must be conducted with care, as a too rapid application of heat would cause the change to take place suddenly, and the whole would ignite.

(*b*) As Metallic Tin.

This process, which is only applicable to tin stone, consists in fusing a known quantity of the pulverized ore with potassium cyanide in a porcelain crucible, when a small button or granules of metallic tin will be obtained on treating the mass with water. The tin is washed, dried, and weighed.

ESTIMATION OF ANTIMONY.

(*a*) As Metallic Antimony.

In the solution, which must contain some excess of hydrochloric acid, a slip of tin is introduced, which will soon precipitate all the antimony as a black powder. The excess of tin is best removed by pouring off the greater part of the liquid and boiling the precipitate with moderately strong hydrochloric acid. When no more evolution of hydrogen is visible, the metal is washed till free from acidity, then again washed with alcohol, collected on a weighed filter, dried, and weighed. Or what is left from the tin may be taken out and carefully freed from the adhering antimony, when boiling with acid is superfluous.

(*b*) As Antimonious Antimonic Oxide.

The acid solution is precipitated with sulphuretted hydrogen, the sulphide collected on a weighed filter, dried at 220° F., and weighed. The total weight

being known, a weighed portion of it is taken for conversion into the oxide, when it can be easily calculated how much oxide the whole of the sulphide would have yielded. The conversion of the sulphide into oxide is best done by mixing it with forty times its weight of pure mercuric oxide and heating gently at first and very strongly afterwards, to drive off the mercury. The remaining SbO_2 is weighed. A platinum crucible may be used, but must first be lined with some mercuric oxide before introducing the mixture. The following calculation is now applied :—

$$\frac{\text{Weight of oxide} \times 122}{154} = \left\{ \begin{array}{l} \text{amount of antimony in the} \\ \text{sample taken for analysis.} \end{array} \right.$$

Another process for the conversion of the sulphide into oxide consists in evaporating a known quantity of the sulphide in a porcelain dish with *fuming* nitric acid. When dry, the residue is ignited, cooled, and weighed.

ESTIMATION OF ARSENIC.

(*a*) As Arsenious Sulphide.

The solution must contain the arsenic as arsenious acid. After adding some HCl, a current of sulphuretted hydrogen is passed through the liquid till the latter acquires a strong smell. The excess of gas is now removed by warming the fluid and passing a current of carbonic anhydride through it. The sulphide is collected on a weighed filter, washed, dried at 212° F., and weighed. The following calculation is then applied :—

$$\frac{\text{Weight of sulphide} \times 150}{246} = \left\{ \begin{array}{l} \text{amount of arsenic in the} \\ \text{sample taken for analysis.} \end{array} \right.$$

(*b*) As Magnesium Ammonium Arseniate.

Arsenious acid is dissolved in some hot solution of sodium carbonate, excess of hydrochloric acid is added, and the fluid *gently* heated with potassium chlorate till it smells distinctly of chlorine, even after half an hour. Arsenic sulphur compounds are dissolved in hot potassium hydrate and treated with excess of chlorine gas to convert them into arsenic acid. The solution of arsenic acid thus obtained by either of the foregoing methods is mixed with large excess of ammonium hydrate, and, after being allowed to cool, precipitated with *magnesia mixture* (a fluid prepared by adding ammonium hydrate to a solution of magnesium sulphate and re-dissolving the precipitate with ammonium chloride). After standing for at least twelve hours, the precipitate is collected on a weighed filter, washed with a mixture of one volume of ammonium hydrate and three volumes of water till free from chlorine, dried for three hours at 220° F. and weighed. If only dried at 212° F. the drying will occupy a considerably longer time. The results are usually a trifle too low. The following calculation is applied :—

$$\frac{\text{Weight of precipitate} \times 150}{380} = \left\{ \begin{array}{l} \text{amount of arsenic in the} \\ \text{sample taken for analysis.} \end{array} \right.$$

ESTIMATION OF COBALT.

As Potassium Cobaltous Nitrite.

Cobalt is most accurately estimated in this form. The solution is concentrated to a small bulk, the excess of acid is neutralized with potash, and excess of potassium nitrite and a little acetic acid (to keep the solution slightly acid to test-paper) are then added. After the lapse of twenty-four hours, all the cobalt will have crystallized out as potassium cobaltous nitrite. This salt is

quite insoluble in the mother liquor, but slightly so in pure water. For the washing, a 10% solution of potassium acetate is used, wherein the salt is also insoluble, and the acetate is afterwards removed by washing with alcohol. A weighed filter is used and after drying and weighing, the following calculation is applied:—

$$\frac{\text{Weight of precipitate} \times 117{\cdot}6}{863{\cdot}6} \left\{ \begin{array}{l} \text{amount of cobalt in the} \\ \text{sample taken for analysis.} \end{array} \right.$$

ESTIMATION OF NICKEL.

As Metal.

The solution is precipitated with excess of sodium hydrate and boiled. The precipitate is washed with boiling water, dried, ignited, and weighed. The ignited residue, or a known portion of it, is now introduced into a weighed glass tube and reduced at red heat by a current of hydrogen. The reduced metallic nickel is afterwards weighed.

ESTIMATION OF MANGANESE.

As Manganoso-manganesic Oxide.

Manganese is best estimated in this form. The solution for analysis, if strongly acid, is neutralized with ammonium hydrate and precipitated by ammonium sulphide. The precipitated manganous sulphide is washed with water containing ammonium sulphide, and dissolved in acetic acid. Chlorine gas is passed through the liquid until all the manganese precipitates as manganic peroxide, which is then collected, washed, and calcined in a weighed crucible to bright redness. This forms Mn_3O_4, the crucible and the contents having been cooled and weighed, the weight of the crucible itself is deducted, and the following calculation employed:

$$\frac{\text{Weight of precipitate} \times 165}{229} = \left\{ \begin{array}{l} \text{weight of manganese in the amount of} \\ \text{substance taken for analysis.} \end{array} \right.$$

ESTIMATION OF ZINC.

As Zinc Oxide.

The solution of the zinc salt (freed from other metals if necessary) is precipitated boiling with sodium carbonate, and the solution boiled well. The precipitate is allowed to settle, washed by decantation with boiling water, filtered out, and dried. It is then introduced into a weighed crucible, ignited for some time at a bright red heat, cooled, and weighed. The ignition changes the precipitated zinc carbonate to oxide, and it is weighed as such. Or the solution is precipitated with ammonium sulphide, the zinc sulphide collected on a filter, washed with dilute ammonium sulphide, dried, ignited, and finally weighed as oxide. This process is useful when only small quantities of zinc are present. The calculation is as follows:—

$$\frac{\text{Weight of precipitate} \times 65}{81} = \left\{ \begin{array}{l} \text{weight of zinc in the quantity} \\ \text{taken for analysis.} \end{array} \right.$$

ESTIMATION OF IRON.

(*a*) As Ferric Oxide.

The solution (freed if necessary from other metals, phosphates, and organic matter) is boiled with a few drops of nitric acid to insure that the whole of the iron is in the ferric state. Excess of ammonium hydrate is added, the whole boiled, and rapidly filtered. The precipitated ferric hydrate is

washed with boiling water, dried, and ignited in a weighed crucible for some time. The crucible and contents are weighed, and the weight of the crucible having been deducted, the following calculation is applied:—

$$\frac{\text{Weight of precipitate} \times 112}{160} = \begin{cases}\text{weight of iron in the quantity of}\\ \text{substance taken for analysis.}\end{cases}$$

In the presence of organic matter such as citric or tartaric acids, the iron must first be separated by precipitation with ammonium sulphide, the precipitate washed with dilute ammonium sulphide, redissolved in hydrochloric acid, boiled, oxidized by potassium chlorate, and then precipitated with ammonium hydrate, as directed.

(*b*) Indirect Estimation by means of Metallic Copper.

When an iron solution is free from metals acted upon by copper, such as cupric, arsenic, and mercury salts, it is first of all, if necessary, completely oxidized with hydrochloric acid and potassium chlorate, and the free chlorine is entirely expelled by prolonged boiling. The solution is now introduced into a flask, and the latter is fitted with a perforated cork provided with a long narrow open glass tube. Before closing the flask a few clean and weighed pieces of metallic copper are introduced. The liquid is now boiled till almost quite colourless (not till faint greenish blue, as said in some works). The solution is then poured out of the flask, and the copper, having been rapidly washed with boiling water, is taken out and rinsed with absolute alcohol. On no account must it be rubbed, notwithstanding it may appear blackish. After drying it is weighed, and the *loss* calculated to iron:—

$$\frac{\text{Loss} \cdot 56}{63 \cdot 5} = \text{amount of iron in the sample taken for analysis.}$$

This process is based upon the fact that ferric chloride, boiled with hydrochloric acid and copper, yields ferrous and cuprous chlorides. This process is not available in the presence of nitric acid.

ESTIMATION OF ALUMINIUM.

As Aluminic Oxide.

It is in this form that aluminium is always estimated. The solution containing the alum or other salt of the metal (which must be free from iron and earthy phosphates) is precipitated with a slight excess of ammonium hydrate, and boiled until it only smells very faintly of ammonia. The precipitated aluminic hydrate thus obtained is filtered out, washed with boiling water, and dried. The dry filter and its contents are transferred to a weighed platinum crucible, and ignited to bright redness for some time, allowed to cool, and weighed. The weight of the crucible having been deducted, the following calculation is then applied:—

$$\frac{\text{Weight of precipitate} \times 55}{103} = \begin{cases}\text{weight of aluminium in the quantity}\\ \text{of substance taken for analysis.}\end{cases}$$

ESTIMATION OF CHROMIUM.

As Chromic Oxide.

Salts of chromium are at once precipitated with ammonium hydrate and the precipitate washed, dried, ignited, and weighed as Cr_2O_3. Soluble chromates are first reduced by means of hydrochloric and sulphurous acids, or, instead of the latter, spirit of wine may be used. The following is the process used for the estimation of chromium in the native chrome-iron ore:—The ore is

reduced to powder, which cannot be done too thoroughly, as a correct analysis will be secured if it be carefully pulverized, and dried at the heat of boiling water. Place in a good-sized platinum crucible 5 grammes of the powdered ore, with 6 grammes potassium acid sulphate; heat for a quarter of an hour, at a temperature slightly in excess of the fusing point of the latter substance; after which (for 20 minutes) increase the heat until the crucible becomes reddened, when sulphuric acid fumes will be evolved. By increasing the temperature still more, the remainder of these fumes will be driven off, and the ferrochromic sulphate partly decomposed. Three grammes pure sodium carbonate must now be added. Fuse, and add, in small portions at a time, 5 grammes potassium nitrate, maintaining for an hour a dull red heat; but for the last fifteen minutes a higher temperature may be allowed. Cool the mass, treat it with boiling water, filter, wash the residue with hot water. (This residue should be tested by digestion in heated hydrochloric acid, and any insoluble portion remaining must be again treated as before). The alkaline solution, which frequently contains, in addition to chromic acid, silicic, titanic, and manganic acids, besides aluminium, must be evaporated on a water bath nearly to dryness in the presence of ammonium nitrate in excess, until all free ammonia is driven off. After water has been added, the silicic and titanic acids, with the aluminic and manganic oxides, will remain insoluble; but the chromic acid is dissolved, and is to be treated as follows:—

The filtrate is acidulated by HCl, mixed with sulphurous acid in excess, and slowly heated to ebullition. Ammonium hydrate being added in slight excess, boil again for a little time, wash the precipitated chromic hydrate repeatedly on a filter, until the washings are entirely free from sulphuric acid. Dry the precipitate, and ignite; when it will be found to contain alkaline chromate, owing to the washing not having removed the whole. Before weighing, boil with water; add a few drops of sulphurous acid, then ammonium hydrate, filter again, dry, and finally ignite in a weighed crucible. The weight of chromic oxide, thus yielded by the amount of the ore taken for analysis, calculated to percentage, gives the value of the sample for commercial purposes.

ESTIMATION OF BARIUM.

As Barium Sulphate.

Barium is estimated by weighing out a known quantity of the sample, dissolving in boiling water, and adding excess of sulphuric acid. The whole is then boiled rapidly for a few minutes, and set aside to settle.

The clear liquor is poured off as closely as possible, and the precipitate collected on a filter of *Swedish paper*, and washed with boiling water. The filter and precipitate are next dried and ignited in a weighed platinum crucible (the precipitate being removed as perfectly as possible from the paper, and the latter first burned separately on the crucible lid, and the ash added to the contents of the crucible, to avoid the reduction of $BaSO_4$ to BaS, by the carbon of the paper). The crucible and its contents having been weighed, and the weight of the crucible deducted, the difference equals the $BaSO_4$, which is now to be calculated for barium, thus:—

$$\frac{\text{Difference} \times 137}{233} = \text{Ba in weight of sample taken for analysis.}$$

ESTIMATION OF CALCIUM.

As Calcium Carbonate or Calcium Oxide.

The solution of the lime salt is mixed with ammonium chloride, and is then made strongly alkaline by ammonium hydrate. Should any precipitate (for

instance, calcium phosphate) form, it is redissolved by means of acetic acid, and any insoluble residue is removed by filtration. Ammonium oxalate is now added in excess. The precipitated calcium oxalate is boiled for a few minutes, filtered, the precipitate washed until free from oxalates; the filter and contents are dried at 212° F. The precipitate is now carefully transferred to a tared platinum crucible, and heated gently at first, but afterwards more strongly, the filter being burnt on the lid until the ash is white, and then placed in the crucible. Finally, the whole is ignited strongly in the blowpipe flame for half an hour, cooled, and weighed. The contents of the crucible are calcium oxide; the oxalate producing first carbonate and then oxide when ignited. The blowpipe flame is requisite to ensure the complete reduction of the carbonate to oxide. Some chemists prefer to moisten the calcium carbonate with a solution of pure ammonium carbonate, evaporating to dryness, heating until no more fumes are evolved, and then weighing as carbonate. The great amount of loss relative to the weight of the precipitate which would accrue if a portion of the carbonate were to become accidentally reduced to oxide, inclines us to prefer the former method. The following calculation is now applied :—

$$\frac{\text{Weight of precipitate} \times 40}{100CaCO_3,\text{ or }56CaO} = \text{calcium in the amount taken for analysis.}$$

ESTIMATION OF STRONTIUM.

As Strontium Carbonate.

The solution containing the strontium compound is precipitated with ammonium carbonate and boiled. The carbonate is collected on a filter, washed with hot water, dried, ignited, and weighed. Acids, such as phosphoric, which form with strontium compounds insoluble in dilute ammonia, must be first removed. The following calculation is applied :—

$$\frac{\text{Weight of the carbonate} \times 87{\cdot}5}{147{\cdot}5} = \left\{\begin{array}{l}\text{weight of strontium in the}\\ \text{sample taken for analysis.}\end{array}\right.$$

ESTIMATION OF MAGNESIUM.

As Magnesium Pyrophosphate.

The solution, which must not be over diluted, is mixed with some ammonium chloride, and then with one-third of its bulk of ammonium hydrate. Should the solution be *very* acid, the excess of acid must first be neutralized by ammonium hydrate. When the solution has entirely cooled, excess of di-sodium hydrogen phosphate is added, and the whole allowed to stand for twelve hours. Care must be taken not to touch the sides of the beaker with the stirring rod, as otherwise particles of the triple phosphate will adhere to them so tenaciously that they can only be removed with great difficulty. The precipitate is collected on the filter and washed with a mixture of one volume of ammonium hydrate and three volumes of water, till the washings are free from chlorine and dried. The precipitate is now detached from the filter and put into a weighed platinum crucible, the filter is burned in the lid, the ash added to the contents of the crucible, and the whole ignited by means of a Bunsen burner; and when a large quantity of phosphate has been obtained finally ignited before the blow-pipe. After weighing, the following calculation is applied :—

$$\frac{\text{Weight of the phosphate} \times 48}{222} = \left\{\begin{array}{l}\text{amount of magnesium in the}\\ \text{sample taken for analysis.}\end{array}\right.$$

It sometimes happens that the phosphate, even after prolonged ignition, is very black. In that case it is, after cooling, thoroughly moistened with nitric acid, carefully dried, and re-ignited, when it will be found to be perfectly white.

ESTIMATION OF POTASSIUM.

(*a*) As Potassium Platino-Chloride.

The solution, which must be free from other metals, but may contain calcium, magnesium, and sodium compounds (as their presence does not interfere with the process), is first of all precipitated with excess of barium chloride, which throws down sulphuric, phosphoric, etc., acids. Barium hydrate or some milk of lime is now added in slight excess, when any magnesia will also be thrown down. To the filtered liquid excess of ammonium carbonate is added, the precipitate is separated by the filter and the fluid evaporated in a platinum crucible to dryness, best on the water-bath. When quite dry it is covered with a platinum lid and gently heated as long as white ammoniacal fumes are visible. The residue, which will now consist of potassium chloride, together with perhaps sodium chloride, is however not quite fit for weighing, and must be purified. This is done by redissolving in water and adding a little ammonium carbonate, when a slight precipitate will form. After filtering, the fluid is evaporated, this time in a weighed platinum basin covered with a weighed lid on the water bath, and when dry the residue is gently heated to faint redness for a minute, and cooled. When no sodium is present it will now be pure potassium chloride and may be weighed as such, and the following calculation applied:

$$\frac{\text{Weight of chloride} \times 39}{74{\cdot}5} = \text{potassium in the sample taken for analysis};$$

but should it contain sodium chloride it is dissolved in the smallest amount of water, transferred to a small porcelain basin, and mixed with a *good* excess of solution of platinic chloride. The whole is evaporated to dryness on a water bath kept at a temperature of about 200°F. When quite dry it is again digested with a few drops of platinic chloride solution, to make sure that all the sodium will be in the state of sodium platino-chloride. This sodium compound and the excess of platinic chloride are now removed by spirit of wine of 60 O.P., the precipitate is collected on a weighed filter, washed with alcohol till the washings appear quite colourless, dried at 212° F., and weighed. The following calculation is now applied:—

$$\frac{\text{Weight of potassium platino-chloride} \times 78}{489} = \left\{\begin{array}{l}\text{weight of potassium in the}\\ \text{sample taken for analysis.}\end{array}\right.$$

(*b*) As Sulphate.

This method is applicable where we have to deal with a potash salt containing a volatile acid. The solution is mixed with excess of sulphuric acid and evaporated in a weighed platinum basin. When fumes of sulphuric acid become visible, the basin is covered over with a lid or foil which has been weighed together with the crucible, and gradually heated till fumes cease. While red-hot the foil is lifted up a little, and a small lump of ammonium carbonate put in the crucible, which operation is repeated after a few minutes. The object of introducing the ammonium carbonate is to remove the last traces of free sulphuric acid. After weighing, the following calculation is applied:—

$$\frac{\text{Weight of the sulphate} \times 78}{174} = \left\{\begin{array}{l}\text{potassium in the sample}\\ \quad\text{taken for analysis.}\end{array}\right.$$

ESTIMATION OF SODIUM.

(*a*) As Sodium Chloride.

Proceed in the same way as for potassium.

$$\frac{\text{Weight of sodium chloride} \times 23}{58 \cdot 5} = \text{weight of sodium in the sample.}$$

(*b*) As Sodium Sulphate.

As for potassium.

$$\frac{\text{Weight of the sulphate} \times 46}{142} = \text{sodium in the sample.}$$

ESTIMATION OF AMMONIUM.

As Ammonium Platino-Chloride.

If the solution contains other basylous radicals, a known quantity of it is distilled with some slaked lime in a suitable apparatus, and the distillate received into dilute hydrochloric acid. About three-fourths is distilled over. The distillate is then evaporated to dryness with excess of pure platinic chloride (free from nitro-hydrochloric acid). The dry residue is now treated with a mixture of two volumes of absolute alcohol and one of ether, collected on a weighed filter, washed with the said ether mixture, dried at 212° F., and weighed. The following calculation is now applied :—

$$\frac{\text{Weight of the double chloride} \times 36}{442} = \left\{\begin{array}{l}\text{ammonium in the quantity}\\ \text{taken for analysis.}\end{array}\right.$$

III. GRAVIMETRIC ESTIMATION OF ACIDULOUS RADICALS.

1. HYDROCHLORIC ACID AND CHLORIDES.

The solution containing the acid or a chloride is precipitated with argentic nitrate. Nitric acid is then added, and the whole warmed and stirred till the liquid is perfectly clear. The precipitate is now treated as directed (see Silver), p. 165. After weighing the chloride, the following calculation is applied :—

$$\frac{\text{Weight of the argentic chloride} \times 36 \cdot 5}{143 \cdot 5} = \left\{\begin{array}{l}\text{hydrochloric acid in the}\\ \text{sample taken for analysis.}\end{array}\right.$$

2. HYDRIODIC ACID AND IODIDES.

3. HYDROBROMIC ACID AND BROMIDES.

4. HYDROCYANIC ACID AND CYANIDES.

The process for each of these acids is practically the same as for hydrochloric acid. The argentic cyanide is, however, collected and weighed upon a weighed filter. The argentic iodide and bromide are treated like the chloride; but *if* a filter is used, it must be a weighed one. The filter is afterwards reweighed, and the increase in weight is the amount of argentic iodide or bromide lost during the washing by decantation. The following calculations are respectively applied :—

For the hydriodic acid—

$$\frac{\text{Weight of the iodide} \times 128}{235} = \left\{\begin{array}{l}\text{weight of hydriodic acid in}\\ \text{the sample taken for analysis.}\end{array}\right.$$

For the hydrobromic acid—

$$\frac{\text{Weight of the bromide} \times 81}{188} = \left\{\begin{array}{l}\text{hydrobromic acid in the}\\ \text{sample taken for analysis.}\end{array}\right.$$

For the hydrocyanic acid—

$$\frac{\text{Weight of the argentic cyanide} \times 27}{134} = \left\{\begin{array}{l}\text{hydrocyanic acid in the}\\ \text{sample taken for analysis.}\end{array}\right.$$

5. ESTIMATION OF AN IODIDE IN THE PRESENCE OF A CHLORIDE AND A BROMIDE.

By **palladium.** The solution, slightly acidified, is precipitated with excess of palladious chloride or nitrate. The whole is then allowed to stand in a warm place for twenty four hours, so that the precipitate may thoroughly settle. The supernatant liquor is poured off, and the precipitate having been collected on a filter, and washed, is placed in a weighed platinum crucible and ignited. The whole is then again weighed, and the weight, less that of the crucible, equals the amount of metallic palladium left after ignition. Now 100 parts of the metal combine with 239.6 parts of iodine in the precipitate, therefore the weight of the metal left after ignition × 2.396 = the amount of iodine in the weight of the sample taken for analysis.

6. MUTUAL ESTIMATION OF Cl, Br, AND I IN THE PRESENCE OF EACH OTHER.

Observation has revealed, that although argentic bromide is converted into the chloride by hydrochloric acid, and the iodide into the bromide by hydrobromic acid, yet the potassium salts of hydriodic acid will decompose, not only argentic bromide, but also argentic chloride; and that potassium bromide also reacts upon argentic chloride.

This being recognised, and a solution of a known quantity of the mixed salts being made, divided into three equal volumes, and slight excess of argentic nitrate added to each, three precipitates are obtained, which are to be washed till free from soluble matter. The first of these must then be dried and weighed. The second digested with KBr, washed, dried, and weighed. The third digested with KI, washed, and also, after being rendered free from moisture, weighed. From these three results the amounts of Cl, Br, and I are to be deduced by a calculation based on the difference of the molecular weight of AgCl, AgBr, and AgI.

The first weighing is—

$$AgCl + AgBr + AgI.$$

The second is—

AgBr + AgI, and is consequently increased as 35.5 is to 80.

The third is entirely AgI, and is consequently increased as 80 is to 127.

7. SULPHIDES

Are best analyzed by fusion with a large excess of a mixture of potassium nitrate and carbonate, extracting the fused mass with water, filtering, acidulating with hydrochloric acid, adding excess of barium chloride, and proceeding as for a sulphate, but calculating at the last to sulphur instead of sulphuric acid. Some sulphides can be dissolved in nitric acid or in aqua regia, both of which convert the sulphur into sulphuric acid, but the fusion is always the most accurate method.

8. SULPHURIC ACID AND SULPHATES.

As Barium Sulphate.

To the solution of the sulphate hydrochloric acid is added, then excess of barium chloride, and the whole boiled. When quite clear, a little more barium chloride is added, to ascertain whether all the sulphuric acid has precipitated. The precipitate is now treated precisely as in the barium estimation and the following calculation applied :—

$$\frac{\text{Weight of precipitate} \times 80}{233} = \left\{ \begin{array}{l} \text{weight of sulphuric anhydride in} \\ \text{the sample taken for analysis.} \end{array} \right.$$

9. NITRIC ACID.

(*a*) In Alkaline Nitrates.

If nitric acid be required to be estimated in, say, ordinary nitre, the sample must first be heated to fusion to remove moisture, and then be quickly powdered. A known quantity of it is now mixed in a platinum crucible with (exactly) 4 times its weight of plumbic sulphate. The mixture is ignited till it ceases to lose weight, and the loss will just represent the amount of nitric anhydride in the sample taken for analysis.

If plumbic sulphate is used, the reaction is represented by the following formula :—

$$PbSO_4 + 2KNO_3 = PbO + K_2SO_4 + 2NO_2 + O.$$

(*b*) By Conversion into Ammonia.

The nitrate is converted into ammonia by the action of nascent hydrogen, thus—

$$HNO_3 + 4H_2 = NH_3 + 3H_2O.$$

The nascent hydrogen may be applied in various ways, as follows :—

1. By distillation with sodium hydrate and metallic aluminium, and receiving the evolved ammonia into a known volume of standard acid.
2. By acting on the nitrate for 12 hours with zinc or iron and dilute sulphuric acid, and then adding excess of sodium hydrate, and distilling off the ammonia into a known volume of standard acid.

In any case, the standard acid used is then volumetrically checked back by standard sodium hydrate, and the excess of acid used over that of alkali gives the amount of standard acid neutralized by the ammonia. This amount, having been multiplied by the strength of the acid in each c.c., is calculated to ammonia. Then—

$$\frac{\text{Ammonia found} \times 54}{17} = \left\{ \begin{array}{l} \text{amount of anhydrous nitric acid in} \\ \text{the quantity taken for analysis.} \end{array} \right.$$

10. PHOSPHORIC ACID AND PHOSPHATES.

This acid is always weighed as magnesium pyrophosphate; but several cases may occur.

(*a*) Alkaline Phosphates.

They are at once precipitated with ammonium hydrate and *magnesia mixture*, and the precipitate is treated as directed under Magnesium. Should they contain the acid as meta or pyro- acid, they must first either be boiled with strong nitric acid for one hour, or be fused with potassium sodium carbonate. After the weighing of the magnesium pyrophosphate the following calculation is applied :—

$$\frac{\text{Weight of precipitate} \times 142}{222} = \left\{\begin{array}{l}\text{phosphoric anhydride in the}\\ \text{sample taken for analysis.}\end{array}\right.$$

(*b*) Phosphoric Acid in the Presence of Lime and Magnesia.

The solution (which must contain orthophosphoric acid, or, failing that, should be boiled with HNO_3 as above) is precipitated with ammonium hydrate, the precipitate re-dissolved in the smallest amount of acetic acid, the lime precipitated with ammonium oxalate, and the phosphoric acid precipitated in the filtrate by adding ammonium hydrate and *magnesia mixture*. Before precipitation this filtrate should be evaporated to a bulk of 3 ounces. This process is suitable for determining the "soluble phosphates" in an artificial manure.

(*c*) Phosphoric Acid in the Presence of Iron and Aluminium.

The solution is mixed with excess of ammonium acetate, boiled, and ferric chloride added till a dark-brown precipitate forms. This is washed with boiling water and redissolved in a small quantity of dilute HCl. About five grammes (or more) of citric acid are now added, and when quite cool a few c.c. of the solution are mixed in a test tube with excess of ammonium hydrate. Should this give a lemon colour, it is all right, but should the colour be brownish, it is a sign that sufficient citric acid has not been added. In that case supersaturate the ammoniacal solution with HCl, mix it again with the bulk of the liquid, and add more citric acid, when the same test is to be again applied. If satisfactory, the tested portion is added to the main liquid, and ammonium hydrate is added to the whole in large excess, and, after cooling, *magnesia mixture*.

(*d*) Separation from All Metals.

If necessary, the acid solution is heated and precipitated with H_2S to remove arsenic. The excess of H_2S is boiled off, and large excess of nitric acid is added. An excess of ammonium molybdate dissolved in nitric acid is now poured in, the liquid boiled, and finally allowed to stand for at least twelve hours in a warm place. The precipitate is filtered off, washed with water containing a little molybdate solution, redissolved in dilute ammonium hydrate, and the phosphoric acid precipitated by *magnesia mixture*. This process is the best for determining the total phosphoric acid in manures, coprolites, etc.

11. ARSENIC ACID AND ARSENIATES

Are estimated precisely like phosphates; but the precipitate of ammonium magnesium arseniate is dried at 220° F. on a weighed filter, as already directed under arsenic. The precipitate thus dried is $2(MgNH_4AsO_4).H_2O$, or, for simplicity of calculation, $MgNH_4AsO_4.\frac{1}{2}H_2O$.

12. CARBONIC ACID.

Direct Estimation in Carbonates.

A carbonate is estimated by the loss of weight it undergoes by the displacement of its carbonic anhydride by an acid. A small and light flask is procured, and fitted with a cork through which passes a tube containing fragments of calcium chloride. A weighed quantity of the carbonate is introduced into the flask with a little water, and a small test-tube about two inches long is filled with sulphuric acid and dropped into the flask, so that being supported in an upright position, none of the acid shall mix with the carbonate. The cork is put in, and the weight of the whole apparatus having been carefully noted, it is inclined so as to allow the acid to run from the small tube into the body of the flask. Effervescence sets in, the carbonate is dissolved, and the CO_2 escaping through the calcium chloride tube, is deprived of any moisture it might carry with it. When all action has ceased, and the whole has cooled, it is once more weighed. The difference between the two weights gives the amount of CO_2 evolved, and then

$$\frac{\text{loss in weight} \times 60}{44} = \text{amount of } CO_3 \text{ radical in the weight of sample taken}$$

13. OXALIC ACID.

(*a*) As Calcium Carbonate.

The solution containing the acid, or its potassium or sodium salt, is made alkaline with ammonium hydrate, and precipitated with calcium chloride. The precipitate is washed till free from *chlorides*, dried, ignited, and finally weighed as carbonate. (See Estimation of Calcium.)

$$\frac{\text{Weight of the carbonate} \times 126}{100} = \left\{ \begin{array}{l} \text{oxalic acid in the sample} \\ \text{taken for analysis.} \end{array} \right.$$

14. TARTARIC ACID.

As Calcium Oxide.

The solution (which must contain no other bases than Ka, Na, or NH_4) is made *faintly* alkaline by ammonium hydrate, and precipitated by excess of calcic chloride. The precipitate is washed, dried, ignited (with the blow pipe) and weighed as calcic oxide.

$$\frac{\text{Weight of lime} \times 150}{56} = \text{tartaric acid in the sample taken for analysis}$$

15. SILICIC ACID.

(*a*) In Soluble Silicates.

By soluble silicates are meant those which are either soluble in water or in hydrochloric acid. The solution (which must contain some free HCl) is evaporated to dryness on the water bath, and the residue dried for an hour at 248° F. After cooling, the mass is moistened with strong HCl, and then boiled with water, thus leaving an insoluble residue of pure silicic acid, which is collected on a filter, washed, dried, ignited, and weighed.

(*b*) In Insoluble Silicates.

These bodies must be decomposed by mixing a weighed quantity of the finely powdered substance with four times its weight of sodium potassium carbonate, and fusing the whole for about half an hour. When alkalies have also to be estimated, barium hydrate is used instead of the double carbonate. The crucible must be well covered during fusion. After cooling, the residue will be found soluble in dilute and warm HCl; if, however, much silica be present, a jelly will form. The whole is now evaporated to dryness and treated as before.

CHAPTER X.

ULTIMATE ORGANIC ANALYSIS.

I. ESTIMATION OF CARBON AND HYDROGEN.

This process is performed by heating a weighed quantity of the substance in a tube with some easily reducible body, such as cupric oxide or plumbic chromate, by which the hydrogen and carbon of the organic body are respectively oxidized into water and carbonic anhydride. These products are passed first through a previously weighed tube containing calcium chloride, which retains the water, and then through a bulb apparatus containing potassium hydrate, which absorbs the carbonic anhydride and has also been previously weighed. After the experiment is finished, the increase in weight of the tubes is calculated thus :—

As H_2O : H_2 : : increase in $CaCl_2$ tube.
As CO_2 : C : : increase in KHO bulbs

The operation takes place in a furnace specially constructed, and known as a combustion furnace. It consists of a series of gas burners by means of which a bright red heat can be gradually applied to the whole length of the tube, which rests in and is enclosed by a bed of fire clay.

The details of the actual process are as follows :—

Cupric oxide is prepared by heating cupric nitrate to bright redness in a crucible; it is reduced to powder while still warm, and preserved in a well-stoppered bottle. A tube of hard Bohemian glass (which does not soften at a red heat) is procured, having a bore of about half an inch and a length of fifteen to eighteen inches. It is closed at one end by heating in the blowpipe flame and drawing it outwards and upwards to a point; sufficient cupric oxide to fill it is measured out, heated to expel any moisture (as it is very hygroscopic) and placed in a well-corked flask to cool. When cold, a little oxide is introduced into the tube; and the organic substance, having been weighed out, is rubbed up in a warm mortar with enough cupric oxide to half fill the tube, and the mixture is quickly transferred to that apparatus, sufficient cupric oxide to nearly fill the tube is then introduced, and lastly a few bright copper turnings are put in. To this charged tube is then attached by means of a good cork, a previously weighed tube containing fragments of dry calcium chloride, and to this is in turn fixed by an indiarubber joint a bulb apparatus also previously weighed and containing solution of potassium hydrate of 1·27 specific gravity. The tube is now placed in the furnace, and the glass attachments supported outside of it by appropriate stands. A little air is sucked out by applying the lips to the end of the potash bulbs, and if the alteration of level thus caused in the liquid is maintained for some time the joints are all perfect; but if not, they must be re-made until perfectly air-tight. Heat is now applied to the front portion of the tube by lighting the first five or six burners, and when that part is quite red-hot the next burner is turned on. The heat is thus applied

gradually, taking care that it is so regulated as to produce a regular slow passage of the evolved gases, so that the bubbles may be distinctly counted as they pass. When the whole tube is heated from end to end and all action has ceased, the drawn-out point is broken, a little perfectly dry air is drawn through the whole to carry the last traces of moisture and carbonic anhydride into the bulbs, which are then detached, weighed, and the increase in weight of each noted.

The following example of the results of the combustion of a little pure sugar will show the calculation :—

Weight of sugar taken	·475	gramme.

Potash bulbs after combustion weighed	79·113	grammes.
„ „ before „ „	78·382	„
Difference, due to CO_2	·731	„

Calcium chloride tube after combustion weighed	23·605	grammes.
„ „ before „ „	23·330	„
Difference, due to H_2O	·275	„

$$\frac{(C)\ 12 \times \cdot 731}{(CO_2)\ 44} = \cdot 1994 \text{ carbon} \qquad \frac{(H_2)\ 2 \times \cdot 275}{(H_2O)\ 18} = \cdot 03056 \text{ hydrogen.}$$

Total sugar taken	·475
Total C and H found	·22996
Difference, due to oxygen	·24504

Or, in percentage—Carbon	41·98
Hydrogen	6·43
Oxygen	51·59
	100·00

When the organic matter is a liquid, it is weighed in a small hermetically sealed tube, and a little oxide having been first put into the combustion tube, the sealed one is dropped in, its end broken by a wire, and the whole of the rest of the oxide poured in. The heat is applied till six or seven inches of CuO are bright red, and then the burner underneath the spot where the tube with the liquid lies, is cautiously applied, so as to volatilize the vapour and cause it to pass over the red-hot cupric oxide and so suffer combustion. Fats and other bodies which cannot be mixed with the oxide are weighed in a small platinum boat, which is dropped in and treated like the tube of liquid already referred to.

Substances which are very carbonaceous and difficult to burn are best mixed with a little plumbic chromate and then the rest of the tube filled with the cupric oxide. Another method is, to produce at the last a stream of pure oxygen by putting a little pounded and perfectly dry potassium chlorate (mixed with a little pure sand to divide it) into the closed end of the combustion tube, then some pure CuO, then CuO plus the substance, and fill up as usual. When the last burner is lit, the potassium chlorate gives off sufficient oxygen to clear the tube of other gases and to aid in the combustion of the last particles.

CHAPTER X.

ULTIMATE ORGANIC ANALYSIS.

I. ESTIMATION OF CARBON AND HYDROGEN.

THIS process is performed by heating a weighed quantity of the substance in a tube with some easily reducible body, such as cupric oxide or plumbic chromate, by which the hydrogen and carbon of the organic body are respectively oxidized into water and carbonic anhydride. These products are passed first through a previously weighed tube containing calcium chloride, which retains the water, and then through a bulb apparatus containing potassium hydrate, which absorbs the carbonic anhydride and has also been previously weighed. After the experiment is finished, the increase in weight of the tubes is calculated thus :—

As H_2O : H_2 : : increase in $CaCl_2$ tube.
As CO_2 : C : : increase in KHO bulbs.

The operation takes place in a furnace specially constructed, and known as a combustion furnace. It consists of a series of gas burners by means of which a bright red heat can be gradually applied to the whole length of the tube, which rests in and is enclosed by a bed of fire-clay.

The details of the actual process are as follows :—

Cupric oxide is prepared by heating cupric nitrate to bright redness in a crucible; it is reduced to powder while still warm, and preserved in a well-stoppered bottle. A tube of hard Bohemian glass (which does not soften at a red heat) is procured, having a bore of about half an inch and a length of fifteen to eighteen inches. It is closed at one end by heating in the blowpipe flame and drawing it outwards and upwards to a point, sufficient cupric oxide to fill it is measured out, heated to expel any moisture (as it is very hygroscopic) and placed in a well-corked flask to cool. When cold, a little oxide is introduced into the tube; and the organic substance, having been weighed out, is rubbed up in a warm mortar with enough cupric oxide to half fill the tube, and the mixture is quickly transferred to that apparatus, sufficient cupric oxide to nearly fill the tube is then introduced, and lastly a few bright copper turnings are put in. To this charged tube is then attached by means of a good cork, a previously weighed tube containing fragments of dry calcium chloride, and to this is in turn fixed by an indiarubber joint a bulb apparatus also previously weighed and containing solution of potassium hydrate of 1·27 specific gravity. The tube is now placed in the furnace, and the glass attachments supported outside of it by appropriate stands. A little air is sucked out by applying the lips to the end of the potash bulbs, and if the alteration of level thus caused in the liquid is maintained for some time the joints are all perfect; but if not, they must be re-made until perfectly air-tight. Heat is now applied to the front portion of the tube by lighting the first five or six burners, and when that part is quite red-hot the next burner is turned on. The heat is thus applied

is ascertained by means of a volumetric solution of sodium hydrate. The difference between the amount of acid originally placed in the bulbs and that remaining free as thus ascertained, evidently corresponds to the amount of sulphuric acid neutralized by the ammonia produced during the combustion. The strength of the acid being known, a simple calculation enables us to ascertain the amount of the nitrogen evolved in the form of ammonia.

The following is a practical example :—

Let an acid be prepared containing 2 grammes of pure hydrogen sulphate (H_2SO_4) in 100 c.c., then 20 c.c. of this acid (the quantity introduced into the bulbs) will correspond to ·138 gramme of ammonia, or ·114 gramme of nitrogen. Let an alkaline solution be so graduated that 100 c.c. will exactly neutralize the 20 c.c. of the standard acid. If we now find that the acid which was in the bulbs after the combustion, requires only 70 c.c. of the alkaline solution, it is evident that $\frac{20 \times 30}{100} = 6$ c.c. were saturated by the ammonia, and the quantity of nitrogen is obtained by the proportion $\frac{·114 \times 6}{20} = ·0342$ gramme of nitrogen.

(*b*) **The process of Dumas.** This consists in measuring the amount of pure nitrogen evolved, and is suitable for certain organic bases and for compounds containing nitrosyl (NO) or nitryl (NO_2) in which the soda lime fails to convert all the nitrogen into ammonia.

The combustion tube (which in this case is twenty six to twenty eight inches long) is packed (1) with six inches of dry sodium hydrogen carbonate ; (2) with a little pure cupric oxide ; (3) with the weighed substance mixed with CuO ; (4) with more pure CuO, and lastly with a considerable length of pure spongy metallic copper, and the whole is closed by a good cork through which passes a bent delivery tube dipping under the surface of mercury in a small pneumatic trough. Heat is first applied to the very end portion of the $NaHCO_3$ until sufficient CO_2 has been given off to entirely drive all the air out of the apparatus, which is ascertained by collecting a little of the gas passing off and seeing that it is entirely absorbed by solution of potassium hydrate. A graduated glass jar is then filled, one-third with strong solution of KHO, and the remainder with mercury, and carefully inverted into the mercury trough so that no air is admitted, and placed over the mouth of the delivery tube. Combustion is now commenced at the front of the tube and gradually carried backwards as usual. The gases evolved are CO_2 and N, the former of which is absorbed by the KHO and the latter collects in the graduated jar. When the heat reaches the back of the tube the remainder of the $NaHCO_3$ is decomposed, and the carbonic anhydride given off chases any trace of nitrogen out of the tube. It only remains to read off the volume of nitrogen, notice the temperature and pressure, calculate to 0° C and 760 mm. bar, and then reduce the volume found to weight.

III. ESTIMATION OF CHLORINE.

In the ordinary combustion of chlorinated compounds it is better to use plumbic chromate than cupric oxide, because in the latter case a volatile cupric chloride would be formed. Chlorine itself is estimated by combustion of the substance in a tube filled with pure calcium oxide, when it displaces oxygen and turns part of the oxide into soluble calcium chloride. After combustion the contents of the tube are digested in water, filtered, excess of argentic nitrate added, and the precipitate washed, dried, and weighed as already directed (see Gravimetric Estimation of Chlorine).

IV. ESTIMATION OF SULPHUR AND PHOSPHORUS.

When substances contain either of these elements, it is best to use plumbic chromate for the estimation of the C and H; or, if cupric oxide be used, then to place a little plumbic oxide in the front of the tube. The sulphur and phosphorus themselves are estimated by fusing in a silver crucible with twelve times the bulk of pure potassium nitrate, a little mixed carbonate and nitrate being first put into the crucible, heated to fusion, and the mixture added a little at a time, waiting between the additions till action ceases. After fusion the sulphur and phosphorus, which have been converted into sulphuric and phosphoric acids respectively, are estimated by dissolving the residue in water and proceeding by precipitation as barium sulphate and magnesium ammonium phosphate respectively. (See Gravimetric Estimation of Sulphuric and Phosphoric Acids.)

CHAPTER XI.

SPECIAL PROCESSES IN ANALYSIS.

UNDER this head it is proposed to give the analysis of some ordinary articles likely to come prominently under the notice of Pharmaceutical Chemists.

I. POTABLE WATER.

The Analysis of Waters Suspected to be Sources of Disease is daily becoming a more important matter, owing to the rapid enlightenment of the public on sanitary questions. It is an operation which every pharmacist should be able to perform.

The following is a sketch of a method of sanitary water analysis which will be found easy to conduct, and is based upon the researches of Messrs. Wanklyn and Chapman, who have contributed much to our knowledge on this subject. The apparatus and reagents required consist of—

1. A tubulated stoppered retort, to hold about 30 ounces, adapted with a piece of indiarubber tubing to a Liebig's condenser.
2. A non-tubulated retort, to hold about 10 ounces, also adapted to a condenser.
3. A burette to contain 10 c.c. graduated in $\frac{1}{10}$ c.c.
4. A Bink's burette, to hold 1000 grains, graduated in $\frac{1}{2}$-decems.
5. A wide-mouth stoppered bottle, of 8 oz. capacity, graduated to hold 1000 grains of water.
6. A platinum evaporating dish, to hold 4 ounces of water without running over.
7. A water and air bath fitted with a centigrade thermometer.
8. A good balance to show $\frac{1}{10}$ of a milligrame.
9. A standard solution of lime, made by dissolving 16 grains of perfectly pure calcium carbonate in dilute hydrochloric acid, evaporating to dryness, again moistening with water, once more drying, and finally dissolving in one gallon of pure distilled water.
10. A standard solution of argentic nitrate, made by dissolving ·479 gramme of the pure salt in a litre of water, each c.c. of which will be equal to $\frac{1}{10}$ of a milligramme of chlorine.
11. A perfectly neutral solution of pure potassium chromate.
12. A solution of 100 grammes pure sodium hydrate, in one litre of water.
13. A cold saturated solution of sodium carbonate which has been boiled for some time.
14. A solution of 8 grammes potassium permanganate, in a litre of water, with 200 grammes of potassium hydrate. The whole is boiled for about an hour, and when cold, made up to one litre with pure distilled water.
15. Some fragments of sheet aluminium, about this size .

16. A standard solution of potash soap (*sapo mollis*, B.P.) in proof spirit of such strength that 32 decems. (320 grains) delivered exactly from the Bink's burette, produce a permanent froth or lather that lasts five minutes when well shaken, in the wide-mouthed bottle, with 1000 grains of the standard lime solution.

The points to be noticed in the sanitary analysis of water are—

Total Hardness,
Permanent Hardness,
Chlorine,
Nitrogen as Nitrates and Nitrites,
Free Ammonia,
Albuminoid Ammonia,
Total Solid Residue,

and these we will consider *seriatim*.

1. **Total Hardness** is supposed to represent the whole amount of lime and other salts which render a water *hard* and unfit for use for culinary and cleansing purposes. It is measured by the quantity of soap which can be rendered insoluble in water by conversion into a lime soap. (*See* Oleates.) The presence of undecomposed soap in watery solution is always recognisable by the permanent white froth which is produced on the surface of the liquid by violent shaking and then setting at rest. If a spirituous solution of soap be added to water containing lime, a compound is formed between the lime and the fatty acids of the soap, which, being insoluble in water, floats to the surface in white flakes, and no permanent froth can be produced until enough soap has been added to thus precipitate all the lime. 1000 grains of the water to be tested are introduced into the wide-mouthed stoppered bottle, and some soap solution is added from the burette. The bottle is closed, and well shaken; and the addition of soap is continued, shaking each time, until a permanent lather is produced which lasts five minutes. The number of test measures (decems of 10 grains of water, as indicated on the burette) of soap solution thus used is then read off, and the following table is referred to as therein directed. After each shaking, the carbonic anhydride which collects in the bottle should be sucked out by means of a glass tube. In cases where a water takes more than 32 measures of soap, 500 grains only must be employed and diluted to 1000 with distilled water before use; the result obtained being multiplied by 2.

Dr. Clarke's Table for taking the Hardness of Water.

Degrees of Hardness.	Test Measures used.	Difference.
0	1·4	1·8
1	3·2	2·2
2	5·4	2·2
3	7·6	2·0
4	9·6	2·0
5	11·6	2·0
6	13·6	2·0
7	15·6	1·9
8	17·5	1·9
9	19·4	1·9
10	21·3	1·8
11	23·1	1·8
12	24·9	1·8
13	26·7	1·8
14	28·5	1·8
15	30·3	1·7
16	32·0	

Should the number of test measures used ($=n$) coincide with any number in the second column, the hardness is seen by glancing at the corresponding

number in the first column. If, however, *n* should come between two numbers, the *lower* of the two must be deducted from *n*, and the difference so obtained divided by the number in the third column opposite to the *higher* of the two. The quotient thus arrived at is to be added to the number in the first column corresponding to the *lower* of the two numbers, and the sum will be the hardness.

EXAMPLE.—Measures used = 20, which falls between 19·4 and 21·3, then $20 - 19{\cdot}4 = {\cdot}6$; and $\frac{{\cdot}6}{1{\cdot}8} = {\cdot}33$; lastly, $\cdot 33 + 9 = 9{\cdot}33$ degrees of hardness.

2. **Permanent Hardness** indicates the amount of calcic and magnesic salts in a state other than carbonate. The calcic and magnesic carbonates are held in solution in water by the carbonic anhydride (carbonic acid gas) dissolved in the fluid. On boiling, this gas passes off, and the carbonates are consequently precipitated, while all other salts remain unaffected. High permanent hardness is bad, because it is an indirect confirmatory evidence of sewage contamination, as showing the presence of sulphates and chlorides, both of which might be derived from such a source. Moreover, it would be impossible to render such a water potable by boiling. 1000 grains of the sample are introduced into a small flask, and a mark made with a file at the surface of the water. It is then briskly boiled for twenty minutes, and made up, when cold, to the mark, with distilled water. The sample thus prepared is put into the bottle, and treated with soap solution, as already directed, and the result noted as permanent hardness.

3. **Chlorine present as Chlorides** is important, as also being a product of the decomposition of sewage matters. It is estimated as follows:—70 c.c. of the water to be tested are placed in a beaker over a sheet of white paper, and brought under the 10 c.c. burette, charged with the standard solution of argentic nitrate. Two drops of the solution of potassium chromate are then added, and the silver solution is very carefully run in, with constant stirring, until the solution in the beaker just changes from yellow to red. This indicates that all the chlorides have been precipitated as argentic chloride. The red-coloured argentic chromate will not form until all the chlorides have been removed; but whenever this is attained, the least excess of silver solution turns the chromate red. Each c.c. of silver solution used will indicate (if 70 c.c. be taken for analysis) $\frac{1}{10}$ of a grain of chlorine per gallon of water. The solutions, both of argentic nitrate and potassium chromate, must be *perfectly neutral.*

4. **Nitrogen existing as Nitrates and Nitrites** is very important, because when sewage decomposes, it produces nitrates as one of the ultimate products of its oxidation. Some waters from chalk soils contain nitrates *naturally*, and therefore, taken by themselves, an excess should not condemn a water; but when coupled with high chlorides and free ammonia and a fair quantity of albuminoid ammonia, they may be taken as an index of previous sewage contamination. Such a water should always be examined again after a heavy rainfall, when it is more than probable that active present contamination will be discovered. 100 c.c. of the sample are introduced into the non-tubulated retort with 100 c.c. of the sodium hydrate solution, and the whole is distilled until a phialful of the distillate ceases to give a colour with $1\frac{1}{2}$ c.c. of Nessler's solution. (See **Mercuric Iodide.**) The retort and its contents are allowed to cool, a fragment or two of sheet aluminium is dropped in, and the neck of the retort closed by a cork, through which passes a V shaped tube, filled with fragments of recently ignited clay tobacco pipe, moistened with hydrochloric acid. After standing for the night, during which the nitrates are reduced to

ammonia by the nascent hydrogen produced from the aluminium and the sodium hydrate, the retort is once more attached to the condenser, and gently distilled until the distillate comes over free from ammonia. The ammoniacal distillate is then made up to a definite bulk, say 500 c.c., with *pure* "ammonia free" distilled water, and the ammonia is estimated by Nessler, as hereafter shown. (See No. 8.) The number of milligrammes of ammonia found is multiplied by 14 and divided by 17, which gives the quantity of nitrogen as nitrates in the 100 c.c. of water examined. This result, multiplied by 10, gives milligrammes per litre, or parts in 1,000,000 parts of water.

5. **Free Ammonia** is a matter which, when in excess, renders a water questionable, especially if it be accompanied by much nitrogen, as nitrates and high chlorides. Under this head is also included the ammonia derived from some very readily decomposable bodies, such as urea, as well as that really present in the state of ammonium salts. A little distilled water is introduced into the tubulated retort, and the condenser having been attached, the heat of a large naked Bunsen burner is applied, and distillation continued until the distillate no longer gives a colour with Nessler. The retort is then emptied out, and 500 c.c. of the water to be tested is introduced, with 10 c.c. of the solution of sodium carbonate. Distillation is then resumed, and continued until the water comes over ammonia-free by Nessler. The distillate is made up to a known bulk, say 500 c.c., and the number of milligrammes of ammonia estimated in it in the usual manner. The result, multiplied by 2, gives milligrammes of free ammonia per litre of water (parts in 1,000,000).

6. **Albuminoid Ammonia.** When nitrogenous organic bodies are heated with a strongly alkaline solution of potassium permanganate, they undergo a limited oxidation, and a portion of their nitrogen is obtained as ammonia. This yield of ammonia has been found to be fairly constant, and is therefore made the measure of actual present sewage or other active deleterious organic contamination. The residue remaining in the retort, after the estimation of the free ammonia, is treated with 50 c.c. of the permanganate solution, and distillation is resumed and carried on until the distillate comes over ammonia free. The distillate is made up as before to 500 c.c. with *pure* distilled water, and the ammonia estimated in it by Nessler. The number of milligrammes thus found, when multiplied by two, gives milligrammes per litre (parts in 1,000,000).*

7. **Total Residue.** The platinum dish is washed, dried, and heated to redness. It is then placed in the air bath at 120° C. for a few minutes; taken out, and quickly cooled in a desiccator, or by placing it on a thick slab of cold iron. After cooling it is quickly and accurately weighed, and 70 c.c. of the water having been introduced it is placed on the water bath, and evaporated to dryness. When dry it is placed in the air bath, heated to 120° C. for an hour, cooled as before, and weighed. It is then returned to the bath for half an hour, cooled, and again weighed; and this is repeated until two successive weighings come out alike. The weight of the empty crucible having been deducted, the difference gives the residue, each milligramme of which represents one grain per gallon.

As a specimen of the mode of stating the results of analysis, and also to show the distinctive characters of a good and a bad water, the following two analyses are appended :—

* The processes, Nos. 4, 5, and 6, should be all first performed with pure distilled water, and the amount of ammonia found be marked on the solution bottles as a *check*, to be deducted afterwards from the results of each actual analysis.

	A Good Ordinary Drinking Water.	A very Bad Water from Kingston.	
Total residue	18·84	115·5	Grains per gallon.
Chlorine	·84	12·13	
Total hardness	10·1	40·0	
Permanent hardness	2·1	18·8	
Nitrogen, as Nitrates, etc.	·82	439·35	Parts per 1,000,000.
Free ammonia	·01	1·18	
Albuminoid Ammonia	·08	·20	

8. **Manufacture and Use of Nessler's Solution.** This solution is thus prepared :—50 grammes of potassium iodide are dissolved in a small quantity of boiling distilled water, in a basin placed on a water bath. Hot saturated solution of mercuric chloride is then added, with constant stirring, until a slight *permanent* red precipitate is produced. The solution thus obtained is filtered and mixed with 200 grammes of potassium hydrate dissolved in the smallest possible quantity of distilled water. When the whole is quite cold, it is made up with cold distilled water to the bulk of one litre ; and 5 c.c. of a cold saturated solution of mercuric chloride having been added, the solution is well shaken, and then left to settle. Lastly, the clear portion is decanted and kept for use.

To use the solution we require—

1. A standard solution of ammonium chloride, made by dissolving ·315 gramme of the pure and dry salt in a litre of distilled water free from ammonia.

2. Two tall cylinders, of clear colourless glass, to contain about 150 c.c. each, and graduated at 100 c.c. ; or a pair of perfectly clear long narrow 4-oz. phials will serve the purpose, which can be graduated by pouring in 100 c.c. of water, and scratching with a file.

3. A pipette graduated to deliver $1\frac{1}{2}$ c.c.

4. Some distilled water, perfectly free from ammonia, prepared by redistilling ordinary distilled water until a phialful of the distillate ceases to give a colour with $1\frac{1}{2}$ c.c. of **Nessler**, and saving the rest of the water remaining in the retort.

5. A sheet of white paper, on a table, placed in a good light near a window without any highly-coloured hangings or decorations.

The solution containing the ammonia (usually a distillate in water analysis) is to be diluted to a definite bulk (say 500 c.c.), with the pure water, till it ceases to give any precipitate, but only a colour, with **Nessler**. One of the cylinders or phials is to be filled to the mark (100 c.c.) with the solution, and $1\frac{1}{2}$ c.c. of **Nessler** added by means of the pipette. The colour is to be noted, after five minutes, by *looking down* through the column of liquid held over the white paper. A little (say 2 c.c.) of the standard ammonia is to be added from the burette to the other phial or cylinder, which is to be filled up to the mark with the pure water; and $1\frac{1}{2}$ c.c. of **Nessler** having been added, the colour is to be observed as before. If the two colours correspond, the amount of ammonia is equivalent to 2 c.c. of the standard solution. If not, the second phial is to be emptied, and another trial made, with more or less standard ammonia, as the colour produced is fainter or darker than that in the first phial. When by repeated experiment the two colours are obtained exactly equal, then the number of c.c. of ammonium chloride solution used in the final attempt is to be read off and multiplied to the total volume of the water distillate. The amount thus obtained is then calculated from the quantity of water taken for analysis to one litre.

II. ANALYSIS OF CINCHONA BARKS.

(a) For Quinine only.

(*B.P. Process for Yellow Bark.*)

Test.—Boil 100 grains of the bark, reduced to very fine powder, for a quarter of an hour in a fluid ounce of distilled water acidulated with ten minims of hydrochloric acid, and allow it to macerate twenty four hours; transfer the whole to a small percolator, and after the fluid has ceased to drop add at intervals about an ounce and a half of similarly acidulated water, until the fluid which passes through is free from colour. Add to the percolate 1 fluid solution of subacetate of lead, until the whole of the colouring matter has been removed, taking care that the fluid remains acid in reaction. Filter and wash with a little distilled water. To the filtrate add about thirty-five grains of potassium hydrate, or as much as will cause the precipitate which is at first formed to be nearly re-dissolved, and afterwards six fluid drachms of pure ether. Then shake briskly, and, having removed the ether, repeat the process twice with three fluid drachms of ether, or until a drop of the ether employed leaves on evaporation scarcely any perceptible residue. Lastly, evaporate the mixed ethereal solutions in a capsule. The residue, which consists of nearly pure quinine, when dry, should weigh not less than two grains, and should be readily soluble in diluted sulphuric acid.

(b) For Mixed Alkaloids.

1. In *Cinchona pallida* (B.P. process).

200 grains of the bark, treated in the manner directed in the test for yellow cinchona bark, with the substitution of chloroform for ether, should yield not less than one grain of alkaloids.

2. In *Cinchona rubra* (B.P. process).

100 grains of the bark, treated in the manner directed in the test for yellow cinchona bark, with the substitution of chloroform for ether, should not yield less than 1.5 grain of alkaloids.

(c) Complete Analysis of Cinchona Bark for Alkaloids.

The following is a more complete process than the official one, and has the additional advantage of rapidity when only pursued as far as the obtaining of the total mixed alkaloids. The second part, involving separation, is more tedious.

Mix 300 grains of powdered bark, dried at 212° F., with milk of lime (75 grains of slaked lime to 750 grains of water). Dry the mixture slowly and then boil it with 7 fluid ounces of rectified spirit. Pour off the clear liquid; boil again with half as much more alcohol; filter, and wash the powder with 3½ ounces more alcohol. From the mixed liquors precipitate the calcium as sulphate by a few drops of diluted sulphuric acid. Filter; distil off the spirit, and pour the residual liquid into a capsule, and heat it on a water-bath, until the spirit is wholly expelled. Filter the remaining liquor, which contains all the alkaloids in the form of acid sulphates, and wash the residue (quinovic acid and fatty matter) with water, slightly acidulated with sulphuric acid. The filtrate and washings, reduced to about ½ fluid ounce, are now treated, while still warm, with caustic soda in slight excess. Wash the precipitate with a very little water; press it between folds of blotting paper, and dry on a water-bath. The weight, divided by three, gives the percentage of the total alkaloids.

Five grammes at least of the residue thus obtained is pulverized, digested in 50 grammes of ether, and filtered, whereby the alkaloids are separated into two groups.

(α) Soluble in ether . . Quinine, Quinicine.
(β) Insoluble in ether . . Cinchonine, Cinchonidine, and Quinidine.

(α) *Part soluble in Ether.*—The ether is evaporated, the residue dissolved in 10 parts of proof spirit, acidulated with one-twentieth of sulphuric acid, and alcoholic iodine added until a precipitate is no longer formed. The quinine is thus precipitated as *herapathite.* One part of herapathite washed, and dried at 100°, represents 0·565 parts of pure quinine. The liquid separated from the herapathite is mixed with an alcoholic solution of sulphurous acid, then neutralized with caustic soda, heated on a water-bath to expel alcohol, and mixed with an excess of soda. The precipitate consists of quinicine, with perhaps traces of quinidine and cinchonidine.

(β) *Part insoluble in Ether.*—The insoluble alkaloids are dissolved in 40 parts of hot water with the aid of a little dilute sulphuric acid, the acid being so adjusted that the solution shall preserve a faint alkaline reaction. To this liquid a solution of Rochelle salt is added, and the whole allowed to remain for twelve hours. The cinchonidine will be found separated as tartrate, which may be collected and dried at 100°. One part of this tartrate represents 0·804 parts of cinchonidine. The filtrate is mixed with a solution of potassium iodide, which precipitates the quinidine as a sandy crystalline powder, provided that the quinidine be not very small in quantity relatively to the cinchonine; otherwise the preciptitate is often resinous. One part of the hydriodide dried at 100° represents 0·718 parts of anhydrous quinidine.

The liquid separated from the quinidine is precipitated by caustic soda whereby the cinchonine is obtained; it is collected and dried as in the previous instances.

III. VALUATION OF A SAMPLE OF OPIUM.

This is dependent on the amount of morphine it contains, and is conducted according to the B.P. process as follows :—

Take of opium 100 grains, slaked lime 100 grains, distilled water 4 ounces. Break down the opium, and steep it in an ounce of the water for twenty-four hours, stirring the mixture frequently. Transfer it to a displacement apparatus, and pour on the remainder of the water in successive portions, so as to exhaust the opium by percolation. To the infusion thus obtained, placed in a flask, add the lime, boil for ten minutes, place the undissolved matter on a filter, and wash it with an ounce of boiling water. Acidulate the filtered fluid slightly with diluted hydrochloric acid, evaporate it to the bulk of half an ounce, and let it cool. Neutralize cautiously with solution of ammonia, carefully avoiding an excess ; remove by filtration the brown matter which separates, wash it with an ounce of hot water, mix the washings with the filtrate, concentrate the whole to the bulk of half an ounce, and add now solution of ammonia in slight excess. After twenty-four hours collect the precipitated morphia on a weighed filter, wash it with cold water, and dry it at 212°. It ought to weigh at least from 6 to 8 grains.

In addition to this official process several others have been proposed, but none without a drawback of some kind. The following is good, if carefully performed :—Take 100 grains of opium, previously dried at 212° F., rub it intimately with three times its weight of coarsely-powdered pumice-stone, and percolate with boiling ether to remove narcotine, colouring matter, and wax. Just moisten with a little spirit, and then extract with water slightly acidulated with acetic acid. The amount of water employed should not, if possible, exceed 5 ounces. Ammonia is now added in the slightest possible excess, and the whole set aside for forty-eight hours, when the morphia will be deposited in crystals on the sides of the glass. The mother liquor is to be poured away, the

morphia purified by re-crystallization from boiling alcohol, and the crystals dried and weighed.

In addition to the assay for morphia, the amount of water should always be determined in a sample of opium, by taking a weighed portion of thin slices, and drying over the water-bath until it ceases to lose weight. Besides these points, the dried opium should be exhausted with cold water, and the residue collected on a weighed filter, and again dried at 212° F. The amount of this residue should not exceed 45 per cent. The addition of gum arabic may be detected by precipitating a solution of opium with normal plumbic acetate, concentrating the filtrate to a low bulk, and precipitating out the gum arabic with alcohol. Genuine opium should contain no starch or tannic acid. Lastly, a portion of opium dried at 212° should be weighed and freely incinerated, when the amount of ash left should not exceed 8 per cent.

IV. ESTIMATION OF EMETINE IN IPECACUANHA

Is very readily performed by volumetric analysis as follows, using a standard solution of mercuric iodide in excess of potassium iodide :—

The test solution is prepared by dissolving 135·46 grains of pure mercuric chloride and 498 grains of potassium iodide in 10,000 grains of water. Each decem (10 fluid grains) of this solution will precipitate $\frac{1}{10000}$ of the molecular weight of emetine, and is thus applied :—

150 grains of ipecacuanha are treated with 15 drops of dilute sulphuric acid, and sufficient rectified spirit of wine added to make the whole bulk up to 1500 grains. The whole is allowed to stand for 24 hours, and 1000 grains are decanted off for analysis. The liquid is evaporated until all the alcohol is driven off, and then brought under the burette containing the test solution, which is run in until it ceases to give a precipitate. The final point of the reaction is ascertained by filtering off a drop or two into a watch-glass placed on black paper, and adding a drop of the reagent, when, if no cloudiness appear, the precipitation of the alkaloid is complete. The number of grain-measures of the test used multiplied by ·0189 gives the amount of alkaloid in 100 grains of the sample.

V. ESTIMATION OF ELATERIN IN ELATERIUM.

(*a*) *B.P. Process.*—Boil 25 grains of elaterium with rectified spirit until exhausted, and filter. Concentrate the solution to a low bulk, and pour it into an excess of warm *liquor potassæ*. When quite cold, filter out the crystals of elaterin which have formed, dry, and weigh, when at least 5 grains should result (20 per cent.).

(*b*) *Improved Process.*—Exhaust 1 gramme of elaterium by percolation with chloroform in a small funnel tube, and then add to the solution an excess of ether. Allow the whole to settle, pour off as completely as possible from the crystals of elaterin, and wash them by decantation with pure ether, collect, dry at a very gentle heat, and weigh.

VI. ESTIMATION OF SCAMMONY RESIN IN SCAMMONIUM.

Take 25 grains (or 2 grammes) and dry in a water-bath until the weight is constant (loss of weight = moisture). Place the dried residue on a weighed filter in a small funnel, and percolate with ether until a portion of the ether on evaporation leaves no residue. Dry the filter and its contents at 212°, and weigh and deduct the weight of the filter. Then deduct the weight of the insoluble matter thus obtained from that of the dried residue, and the difference

is scammony resin. The residue is to be then examined for starch and mineral matter.

VII. ESTIMATION OF THE ALCOHOLIC STRENGTH OF SPIRITS, WINES, AND TINCTURES.

If the sample be simply a dilute spirit which leaves no residue upon evaporation, the percentage may be ascertained by taking the specific gravity, thus: A flask is taken, capable of holding exactly 1000 grains of distilled water at 60° F., and after being carefully and exactly counterpoised in a balance, is filled with the spirit previously brought to a temperature of 60° F. If a specific gravity bottle, as generally used in analysis, be employed, it must be filled perfectly, and when inserting the stopper, it should be allowed to sink by its own weight; then, after careful examination to see that no air bubbles remain, the flask is wiped dry and the weight taken. Immediately this is done, the temperature of the contents must be determined, and if not 60° F., the flask must be refilled, placed in a vessel of water at 60° F. for a few minutes, the stopper inserted, and the weight of the dried flask and contents determined as before. When the weight at 60° F. is known, reference is made to the following table, to ascertain the corresponding percentage of alcohol.

In taking such specific gravities it is of great importance to perform the operation say three times, and take the average of the three determinations, as a very small error makes a great difference in the commercial value of the sample under examination.

If the sample be a wine or tincture containing matters in solution, the following course must be adopted:—2000 grains must be weighed out, rendered neutral by sodium carbonate, if acid, and immediately transferred to a retort. This must be adapted (in any convenient manner so as to render the joint air-tight) to a Liebig's condenser, and the heat of a water-bath being applied, the spirit distilled over into a previously weighed flask, the condenser being kept cool by a constant slow stream of cold water passing through it. When about nine-tenths of the liquid in the retort have distilled over, the flask and contents are weighed, and the weight of the flask deducted. The temperature of the spirit having been rendered correct (60° F.), the specific gravity must be determined as above. The corresponding percentage of alcohol having been ascertained from the tables, the calculation is as follows:—

$$\frac{\text{Percentage of alcohol in distillate} \times \text{weight of distillate}}{2000} = \left\{\begin{array}{l}\text{percentage by}\\ \text{weight of alco-}\\ \text{hol in sample.}\end{array}\right.$$

EXAMPLE.—2000 grains of sherry (*vinum Xericum*) taken and distilled. The distillate weighed 1772·8 grains, and the specific gravity was ·9711, answering to 20·4 per cent. by weight of alcohol.

$$\text{Then, } \frac{1772{\cdot}8 \times 20{\cdot}4}{2000} = \left\{\begin{array}{l}\text{18·08 per cent. of absolute alcohol by weight in}\\ \text{sample, which is too high for a natural sherry.}\end{array}\right.$$

le of the Proportion by Weight of Absolute or Real Alcohol in 100 parts of Spirits of different Specific Gravities (Fownes).

Sp. Gr. at 60° F. (15·5° C.)	Percentage of real Alcohol.	Sp. Gr. at 60° F. (15·5° C.)	Percentage of real Alcohol.	Sp. Gr. at 60° F. (15·5° C.)	Percentage of real Alcohol.
0·9991	0·5	0·9511	34	0·8769	68
0·9981	1	0·9490	35	0·8745	69
0·9965	2	0·9470	36	0·8721	70
0·9947	3	0·9452	37	0·8696	71
0·9930	4	0·9434	38	0·8672	72
0·9914	5	0·9416	39	0·8649	73
0·9898	6	0·9396	40	0·8625	74
0·9884	7	0·9376	41	0·8603	75
0·9869	8	0·9356	42	0·8581	76
0·9855	9	0·9335	43	0·8557	77
0·9841	10	0·9314	44	0·8533	78
0·9828	11	0·9292	45	0·8508	79
0·9815	12	0·9270	46	0·8483	80
0·9802	13	0·9249	47	0·8459	81
0·9789	14	0·9228	48	0·8434	82
0·9778	15	0·9206	49	0·8408	83
0·9766	16	0·9184	50	0·8382	84
0·9753	17	0·9160	51	0·8357	85
0·9741	18	0·9135	52	0·8331	86
0·9728	19	0·9113	53	0·8305	87
0·9716	20	0·9090	54	0·8279	88
0·9704	21	0·9069	55	0·8254	89
0·9691	22	0·9047	56	0·8228	90
0·9678	23	0·9025	57	0·8199	91
0·9665	24	0·9001	58	0·8172	92
0·9652	25	0·8979	59	0·8145	93
0·9638	26	0·8956	60	0·8118	94
0·9623	27	0·8932	61	0·8089	95
0·9609	28	0·8908	62	0·8061	96
0·9593	29	0·8886	63	0·8031	97
0·9578	30	0·8863	64	0·8001	98
0·9560	31	0·8840	65	0·7969	99
0·9544	32	0·8816	66	0·7938	100
0·9528	33	0·8793	67		

VIII. EXAMINATION OF A TINCTURE FOR THE PRESENCE OF METHYLATED SPIRIT.

The process usually adopted by pharmacists is that proposed by Mr. Miller. For the purpose of testing tinctures, they must first be distilled until the greater part of the spirit has passed over. The distillate is treated as follows :—

A small flask is fitted with a cork and a tube having two right angular bends, and in it is put,—

1. About half a drachm of the spirituous liquid required to be tested.
2. An equal quantity of potassium dichromate, and of pure sulphuric acid.
3. Four or five times as much water.

The mixture, after standing for twenty minutes, is distilled at a gentle heat, until nearly the whole has passed over. Sodium carbonate having been added to the distillate till it is slightly alkaline, the liquid is evaporated in a porcelain basin to about half its [illegible] and having been acidulated slightly by acetic acid, is transferred to a test-tube, heated gently with twenty drops of a five per

cent. solution of argentic nitrate for a few minutes, when any decided opacity (due to the discoloration of the fluid and the separation of a blackish precipitate of metallic silver), indicates the presence of methyl hydrate in the sample thus tested. In the oxidation of ordinary alcohol a mere trace of formic acid is formed by secondary decomposition, consequently a distinct precipitate must be obtained before the spirit can, with certainty, be pronounced to be methylated.

The operation of the above process depends on the fact that by oxidation with sulphuric and potassium dichromate, aldehyds and acids are produced, which, by being boiled with sodium carbonate, yield sodium acetate and formate, the former from the ordinary "alcohol" and the latter from the wood spirit. Upon the addition of argentic nitrate, argentic formate is produced, which is easily reduced by boiling to metallic silver, while argentic acetate is not so affected.

When this process has to be applied to sweet spirit of nitre, the ethyl nitrite must be first got rid of, as follows:—

Take a little of the spirit and place it in a bottle with some dry potassium carbonate, and shake up. Let it settle, and take about two drachms of the strong spirit which separates. Saturate this with calcium chloride, and distil on a water-bath, rejecting the distillate (ethyl nitrite, etc.). Add a little water to the contents of the retort and distil again, when the pure spirit will come over, and a portion may then be tested as above directed.

IX. ESTIMATION OF FREE SULPHURIC ACID IN VINEGAR.

(*a*) *B.P. Process.*—If ten minims of solution of barium chloride be added to a fluid ounce of the vinegar, and the precipitate, if any, be separated by filtration, a further addition of the test will give no precipitate (absence of more than $\frac{1}{10}$ per cent. of sulphuric acid).

(*b*) *Improved Method.*—The official test given above is entirely valueless in the case of vinegars containing much sulphate, from being made with water rich in that ingredient; it is therefore necessary, if the vinegar appear to be adulterated when thus tried, to proceed as follows: 50 c.c. of the vinegar are mixed with 25 c.c. of volumetric solution of sodium hydrate, made decinormal by diluting the official volumetric solution to ten times its bulk with water. The whole is evaporated to dryness, and incinerated at the lowest possible temperature. 25 c.c. of decinormal solution of sulphuric acid (made to exactly balance the sodium hydrate solution) are now added to the ash, the liquid heated to expel CO_2, and filtered. The filter is washed with hot water, and the washings having been added to the filtrate, litmus solution is added, and the amount of free acid ascertained by running in decinormal soda from a burette. The number of c.c. of soda thus used multiplied by ·0049 gives the amount of free sulphuric acid in the vinegar. This process depends on the fact that *whenever the ash of vinegar has not an alkaline reaction, free mineral acid was undoubtedly added.*

X. ANALYSIS OF URINE.

The following are the chief points on which information is usually required by the physician who submits a urine for examination to a chemist:—

1. Take the specific gravity, which should range from 1·015 to 1·025 at 60°F.

Note.—In diabetes the gravity is too high, sometimes reaching 1·060, while in albuminuria it is abnormally low, even occasionally falling to 1·005.

2. Examine the reaction, which should be very faintly acid.

Set a portion to settle in a long glass, and examine the deposit under the microscope for calcium oxalate or phosphate, uric acid or urates, pus, casts of kidney tubes, etc., etc.

Note.—The nature of the deposit may also be confirmed chemically as follows :—

(*a*) Warm the urine containing the sediment, when, if the latter should dissolve, it consists entirely of urates. In this case let it once more crystallize out, and examine it by the ordinary course for Ca, Na, and NH_4, to ascertain the bases.

(*b*) If the deposit be not dissolved by heating, let it settle, wash once by decantation with *cold* water, and warm with acetic acid. Phosphates will dissolve, and may be reprecipitated from the solution by excess of NH_4HO, filtered out, well washed with boiling H_2O, dissolved in $HC_2H_3O_2$ and examined for Ca or Mg by the usual course for these metals in presence of PO_4.

(*c*) If the deposit be insoluble in acetic acid, warm it with HCl. Any soluble portion is calcium oxalate, which may be reprecipitated by NH_4HO.

(*d*) If the deposit be insoluble in HCl it is probably uric acid. In this case apply the *murexid* test as follows. Place it in a small white dish, remove moisture by means of a piece of bibulous paper, add a drop or two of strong HNO_3 and evaporate to dryness at a gentle heat. When cold add a drop of NH_4HO, which will produce a purple colour deepened to violet by a drop of KHO.

4. Test for albumen, as follows :—

(*a*) Take a drachm of the urine and add from 10 to 15 drops of strong nitric acid, when any albumen present will be coagulated, and form a distinct cloud.

(*b*) *Millon's Mercurial Colour Test.*—Take equal parts by weight of Hg and strong HNO_3 and dissolve by gentle heat, adding afterwards 2 parts of hot H_2O. Set the whole aside to crystallize, pour off the mother liquor and keep it for use. The solution added to albuminous urine turns it red, and the colour deepens by warming nearly to boiling.

(*c*) *Bödeker's Method.*—Take a drachm of the urine, acidulate it with acetic acid, and add some potassium ferrocyanide drop by drop till a clear excess has been added. If during the addition a precipitate forms, albumen is to be suspected.

Note.—Of these three methods, (*a*) is decidedly the most reliable.

(*d*) If the result of (*a*) shows the presence of albumen, take a weighed quantity of the urine, and allow it to drop into boiling water acidulated with acetic acid. Collect the precipitate on a tared filter, wash with boiling water, dry at 212°, weigh, and deduct the weight of the filter, when the balance = albumen in the weight of urine operated upon.

5. Test for grape sugar, as follows :—

(*a*) *Moore's Test.*—Acidulate with acetic acid, boil, and filter out any albumen if necessary. Then mix the filtrate with equal parts of *liquor potassæ* and heat to boiling, when ordinary urine will turn brownish-red, but saccharine urine will become dark brown or black.

(*b*) *Trommer's Test.*—Add to some urine in a test-tube 5 to 10 drops of solution of cupric sulphate (gr. x. in ℥i.), then add solution of

KHO until the precipitate first formed is redissolved. Slowly heat the solution till nearly boiling, when, if sugar be present, a brick-red precipitate of cuprous oxide forms.

(c) *Fehling's Test.*—Render the urine alkaline with potassium hydrate, and filter to remove any phosphates, etc., which may precipitate. Boil the filtrate with Fehling's solution of copper (see page 159), and if a red precipitate should form, sugar is present.

(a) If the presence of sugar be thus ascertained, estimate its amount by taking 10 grammes of the urine and diluting it with water to 100 c.c. Place this solution into a burette, and run it gradually into 10 c.c. of Fehling's solution, kept boiling in a basin as directed under the volumetric analysis of sugar, page 160. The number of c.c. of urine used will contain ·01 of grape sugar, and then $\frac{100 \times \cdot 01}{\text{c.c. used}}$ = sugar in the 10 grammes of urine taken.

6. Test for Bile, as follows :—

(a) *Gmelin's Test for Bile Pigments.*—Place a drachm of nitric acid in a test-tube and cautiously pour upon it an equal volume of the urine. In the presence of bile a play of colours from green to violet, blue, and red will be observed where the liquids touch.

(b) *Pettenkofer's Test for Biliary Acids.*—Mix equal parts of urine and sulphuric acid, add one drop of saturated syrup, and apply a gentle heat. If biliary acids be present, the colour will change from cherry-red to deep purple.

Note.—Bilious urine is usually of a brownish-green colour.

7. Test for Urea, as follows :—

(a) Separate any albumen (as directed in Moore's test) if necessary, and evaporate an ounce of the urine to a syrupy consistence on the water-bath. When cold add nitric acid, drop by drop, till crystals of nitrate of urea cease to deposit.

(b) Estimate the amount of urea by mercuric nitrate as directed at page 160, or, if inconvenient, ascertain roughly whether the urea is in excess as follows : Take a drop of the clear urine, place it on a glass slide, add a drop of nitric acid, and place under the microscope. If flat rhombic or hexagonal plates of nitrate of urea be thus formed, without concentration of the urine, then the urea is in excess of the natural amount.

8. Test for Uric Acid by mixing one ounce of the urine with one drachm of hydrochloric acid in a beaker, and set aside for some hours. The uric acid will be deposited in reddish-brown crystals, which may, if desired, be weighed and proved by the *murexid* test (page 197).

9. Test for Phosphates, as follows :—

(a) Add to one ounce of the urine a slight excess of ammonium hydrate, and boil. $Ca_3 2PO_4$ and $MgNH_4PO_4$ will both be precipitated, and the precipitate, if more than a distinct cloud, should be filtered out, dissolved in HCl, and analyzed by the ordinary process already given for phosphates.

(b) After filtering out the earthy phosphates as above, alkaline phosphates may be tested for by adding *magnesia mixture* to the filtrate and getting the usual precipitate of $MgNH_4PO_4$ after standing some hours in a cold place. This may be estimated if required as usual.

10. Test for Sulphates, as follows :—
Acidulate a weighed quantity of the urine with HCl, warm, and add excess of $BaCl_2$. If the precipitate appear too copious, estimate as usual.

11. Test for Chlorides, as follows :—
Acidulate a little of the urine with HNO_3 and add excess of argentic nitrate. If the precipitate thus produced looks very large, a weighed quantity of the urine should be mixed with some potassium nitrate, evaporated to dryness, and fused. The residue is then to be dissolved in water and the chlorine estimated volumetrically by argentic nitrate with potassium chromate as the indicator.

12. *Blood* is best seen under the microscope; but urine containing it has always a very characteristic smoky appearance. A test for blood is to add tincture of guaiacum and ethereal solution of hydrogen peroxide, which produce a sapphire blue; but such colour of itself should not be taken as positive proof without the blood discs being also visible under the microscope.

XI. ANALYSIS OF URINARY CALCULI.

The following table will show at a glance the composition and methods of proving the various calculi.

I. Calculi, fragments of which, heated to redness on platinum, entirely burn away.

NAME.	PHYSICAL CHARACTERS.	CHEMICAL CHARACTERS.
Uric Acid $C_5N_4H_4O_3$	Brownish-red; smooth or tuberculated; concentric laminæ (common)	Insoluble in water; soluble in KHO by heat, but evolves no NH_3; Dissolves with effervescence in HNO_3 and the residue on evaporating the solution is red and gives the *murexid* test.
Ammonium Urate	Clay-coloured; usually smooth, and rarely with fine concentric laminæ (uncommon)	Soluble in hot water; soluble in heated KHO, evolving NH_3. Behaves with HNO_3 like uric acid.
Cystine $C_3H_7NSO_2$	Brownish-yellow, semi-transparent and crystalline (very uncommon)	Insoluble in H_2O, alcohol, and ether. Soluble in NH_4HO and depositing, when allowed to evaporate spontaneously, hexagonal plates. When heated, gives off odour of CS_2.
Xanthin $C_5H_4N_4O_2$	Pale polished brown surface (very uncommon)	Soluble in KHO; soluble in HNO_3 *without effervescence*, and the solution leaves on evaporation a deep yellow residue.

II. Calculi, fragments of which, heated to redness on platinum, do not burn away.

Name.	Physical Characters.	Chemical Characters.
Calcium Oxalate, *mulberry calculus*, CaC_2O_4	Deep brown, hard and rough; thick layers (common)	Insoluble in acetic acid, but soluble without effervescence in HCl; heated to redness, it is converted into $CaCO_3$ which dissolves with effervescence in acetic acid, and the solution gives a white precipitate with $(NH_4)_2C_2O_4$. Heated strongly before the blow-pipe, CaO remains, which, when moistened, is alkaline to test-paper.
Tricalcium Phosphate, *bone-earth calculus*, $Ca_3 2PO_4$	Pale brown, with regular laminæ (uncommon)	Infusible before the blow-pipe, and residue, when moistened, is not alkaline. Soluble in HCl, and the solution gives a *gelatinous* precipitate with excess of NH_4HO.
Magnesium Ammonium Phosphate, *triple phosphate calculus*, $MgNH_4PO_4$	White, brittle, crystalline, with an uneven and not usually laminated surface (uncommon)	Fusible with difficulty before the blow-pipe, evolving NH_3, and residue not alkaline. Soluble in HCl, and solution gives white *crystalline* precipitate with NH_4HO.
Mixed Phosphates of Ca, Mg, and NH_4, *fusible calculus*	White, and rarely laminated	Readily fusible before the blow-pipe. Soluble in acetic acid, and solution gives a white precipitate with $(NH_4)_2C_2O_4$, and the filtrate from that precipitate gives a white precipitate with excess of NH_4HO.

APPENDIX.

WEIGHTS AND MEASURES OF THE METRICAL SYSTEM.

From the British Pharmacopœia of 1867.

Weights.

1 Milligramme	=	the thousandth part of one gramme, or	0·001 gramme.
1 Centigramme	=	the hundredth ,,	0·01 ,,
1 Décigramme	=	the tenth ,,	0·1 ,,
1 Gramme .	=	weight of a cubic centimètre of water at 4°C.	1·0 ,,
1 Décagramme	=	ten grammes	10·0 ,,
1 Hectogramme	=	one hundred grammes	100·0 ,,
1 Kilogramme	=	one thousand grammes	1000·0 (1 kilo.).

Measures of Capacity.

1 Millilitre	=	1 cubic centimètre,	or the measure of	1	gramme	of water.
1 Centilitre	=	10 ,,	,,	10	,,	,,
1 Décilitre	=	100 ,,	,,	100	,,	,,
1 Litre .	=	1000 ,,	,,	1000	,,	(1 kilo.).

Measures of Length.

1 Millimètre	=	the thousandth part of one mètre or,	0·001 mètre.
1 Centimètre	=	the hundredth ,,	0·01 ,,
1 Décimètre	=	the tenth ,,	0·1 ,,
1 Mètre .	=	the tenth-millionth part of a quarter of the meridian of the earth.	

WEIGHTS AND MEASURES OF THE BRITISH PHARMACOPŒIA OF 1867.

Weights.

1 Grain	gr.			
1 Ounce	oz.	. .	=	437·5 grains.
1 Pound	lb.	= 16 ounces	=	7000 ,,

Measures of Capacity.

1 Minim	min.		
1 Fluid Drachm	fl. drm.	=	60 minims.
1 Fluid Ounce	fl. oz.	=	8 fluid drachms.
1 Pint	O.	=	20 fluid ounces.
1 Gallon	C.	=	8 pints.

Measures of Length.

1 Line = $\frac{1}{12}$ inch.
1 Inch = $\frac{1}{39\cdot1393}$ seconds-pendulum.
12 ,, = 1 foot.
36 ,, = 3 feet = 1 yard.

Length of pendulum vibrating seconds of mean time in the latitude of London, in a vacuum at the level of the sea. } 39·1393 inches.

(1 cubic inch of distilled water at 62° F. and 30 inch Barom. = 252·458 grains.)

Relations of Measures to Weights.

1 Minim is the measure of		0·91	grain of water.
1 Fluid Drachm	,,	54·68	grains of water.
1 Fluid Ounce	,, 1 ounce, or	437·5	,,
1 Pint	,, 1·25 pound, or	8750·0	,,
1 Gallon	,, 10 pounds, or	70,000·0	,,

COMPARISON OF FRENCH AND ENGLISH MEASURES. By Dr. Warren De La Rue.

MEASURES OF LENGTH.

	In English Inches.	In English Feet, = 12 Inches.	In English Yards, = 3 Feet.	In English Fathoms, = 6 Feet.	In English Miles, = 1760 Yards.
Millimètre	0·03937	0·0032809	0·0010936	0·0005468	0·0000006
Centimètre	0·39371	0·0328090	0·0109363	0·0054682	0·0000062
Decimètre	3·93708	0·3280899	0·1093633	0·0546816	0·0000621
Mètre	39·37079	3·2808992	1·0936331	0·5468165	0·0006214
Décamètre.	393·70790	32·8089920	10·9363310	5·4681655	0·0062138
Hectomètre	3937·07900	328·0899200	109·3633100	54·6816550	0·0621382
Kilomètre	39370·79000	3280·8992000	1093·6331000	546·8165500	0·6213824
Myriamètre	393707·90000	32808·9920000	10936·3310000	5468·1655000	6·2138244

1 inch = 2·539954 Centimètres. 1 Yard = 0·91438348 Mètre.
1 Foot = 3·0479449 Décimètres. 1 Mile = 1·6093149 Kilomètre.

MEASURES OF SURFACE.

	In English Square Feet.	In English Sq. Yards, = 9 Square Feet.	In English Poles, = 272·25 Sq. Feet.	In English Roods, = 10,890 Sq. Feet.	In English Acres, = 43,560 Sq. Feet.
Centiare, or square mètre . .	10·7642993	1·1960333	0·0395383	0·000988457	0·0002471143
Are, or 100 square mètres . .	1076·4299342	119·6033260	3·9538290	0·098845724	0·0247114310
Hectare, or 10,000 sq. mètres .	107642·9934183	11960·3326020	395·3828959	9·884572398	2·4711430996

1 Square Inch = 6·4513669 Square Centimètres. 1 Square Yard = 0·83609715 Square Mètre, or Centiare.
1 Square Foot = 9·2899683 Square Décimètres. 1 Acre = 0·404671021 Hectare.

MEASURES OF CAPACITY.

	In cubic inches.	In cubic feet, = 1728 cubic inches.	In pints, = 34·65923 cubic inches.	In gallons, = 8 pints, = 277·27384 cubic inches.	In bushels, = 8 galls., = 2218·19072 cubic inches.
Millilitre, or cubic centimètre .	0·06103	0·000035	0·00176	0·0002201	0·0000275
Centilitre, or 10 cubic centimètres	0·61027	0·000353	0·01761	0·0022010	0·0002751
Décilitre, or 100 cubic centimètres	6·10271	0·003532	0·17608	0·0220097	0·0027512
Litre, or cubic décimètre . . .	61·02705	0·035317	**1·76077**	0·2200967	0·0275121
Décalitre, or centistère	610·27052	0·353166	17·60773	2·2009668	0·2751208
Hectolitre, or décistère . . .	6102·70515	3·531658	176·07734	22·0096677	2·7512085
Kilolitre, or stère, or cubic mètre	61027·05152	35·316581	1760·77341	220·0966767	27·5120846
Myriolitre, or décastère . . .	610270·51519	353·165807	17607·73414	2200·9667675	275·1208459

1 cubic inch = 16·386176 cubic centimètres. 1 cubic foot = 28·315312 cubic décimètres. 1 gallon = 4·543358 litres.

MEASURES OF WEIGHT.

	In English grains.	In troy ounces, = 480 grains.	In avoirdupois lbs., = 7000 grains.	In cwts., = 112 lbs., = 784,000 grains.	Tons, = 20 cwts., = 15,680,000 grains.
Milligramme	0·01543	0·000032	0·0000022	0·0000000	0·0000000
Centigramme	0·15432	0·000322	0·0000220	0·0000002	0·0000000
Décigramme	1·54323	0·003215	0·0002205	0·0000020	0·0000001
Gramme	**15·43235**	0·032151	0·0022046	0·0000197	0·0000010
Décagramme	154·32349	0·321507	0·0220462	0·0001968	0·0000098
Hectogramme.	1543·23488	3·215073	0·2204621	0·0019684	0·0000984
Kilogramme	15432·34880	32·150727	2·2046213	0·0196841	0·0009842
Myriogramme.	154323·48800	321·507267	22·0462126	0·1968412	0·0098421

1 grain = 0·064799 gramme. 1 troy oz. = 31·103496 grams. 1 lb. avoirdupois. = 0·453593 kilogr. 1 cwt. = 50·802377 kilogrs.

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